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COMPARISON OF NITROGEN AND SULPHUR MINERALIZATION IN SOILS

by

KWASI MAWUEGA SETSOAFIA

(C)

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

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M. Nyborg
.....
Supervisor

.....

.....

.....

Date June 1, 1983

This thesis is dedicated
to the memory of my
father whose devotion
and encouragement has
made my education
possible.

ABSTRACT

In view of the rather constant N:S ratio in many soils the mineralization of S is often considered to follow directly that of N. The purpose of this study was to examine the relationship between N and S dynamics in surface horizons of several soils in Alberta.

Two pairs of surface virgin and cultivated soils were sampled from each of the three soil zones (i.e Brown, Dark Brown and Black) of the Chernozemic Order. Two other pairs of surface soils representing grain-fallow and continuous cropping rotations from the Breton plots(Gray Luvisol) were also sampled. These soil samples were used (i) to compare the mineralization of N and S during continuous incubation with that mineralized during intermittent incubation; and (ii) to assess changes in total N, potentially mineralizable N,(No), total S, C-bonded S (C-S) and HI-reducible S due to long-term natural mineralization processes.

Mineralization of both N and S by the continuous incubation method was found to be irregular with time. Results using the leaching and incubation technique showed that mineralization of N followed first order kinetics while that of S followed zero order kinetics.

In the Chernozemic soils, No values were higher in the virgin soils(77.7 to 286 ug N/g soil) than in the cultivated soils (51.3 to 147 ug N/g soil) with No of soils from Brown<Dark Brown<Black soil zones. Values for mineralization rate constant,k,i.e. fractional loss of No per week were

higher in the cultivated soils(0.061 to 0.097 week^{-1}) than the virgin soils(0.041 to 0.093 week^{-1}) and decreased with soil zone in the following order: Brown>Dark Brown>Black soil zones. In the Breton plots, mean No value(102 ug N/g soil) in the continuous cropping plots was higher than the mean No value(68 ug N/g soil) in the grain-fallow rotation plots. The mean k value(0.072 week^{-1}) in the latter plots was higher than the mean k value(0.067 week^{-1}) in the former plots.

Mean losses of No with cultivation(32.6 to 37.9%) were higher than those of total N(17.0 to 19.5%) in the Chernozemic soils. In the Breton plots, mean difference in total N(36.1%) between continuous cropping and grain-fallow rotation plots was slightly higher than the mean difference in No(33.5%).

Results using the incubation and leaching technique showed that a labile fraction exists for N but not S. In contrast, long-term natural mineralization processes indicated that (i) C-bonded S was depleted faster than HI-reducible S; (ii)Mean difference in HI-reducible S between continuous cropping and wheat-fallow rotation plots was higher than mean difference in C-bonded S and; (iii) the behaviour of C-bonded S but not that of HI-reducible S was similar to that of No. Therefore HI-reducible S is not necessarily the more active component of organic S.

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I. INTRODUCTION

Mineralization of nitrogen and sulphur from soil organic matter is important for maintaining nutrient supplies to crops. From the standpoint of fertilizer management in agriculture it would be helpful to know in advance the quantity of these nutrients a crop will derive from mineralization of organic forms during a growing season. Optimal use of fertilizer can be achieved only if the nutrient supplying power is considered in making fertilizer recommendations.

Crop yields under extensive agriculture are often directly proportional to the N released from organic matter. The other nutrients are equally important but N is required in larger amounts and is more likely to be deficient (Campbell,1978). However, in soils where N is not the nutrient limiting plant growth, a limitation of sulfur as well as of other elements could be expected if plant growth is intensified(Postgate,1974). Thus much more effort appears to have been directed towards devising a suitable laboratory method for assessing the N supplying power of soils than S or any other element. Attempts to devise a method for predicting mineralizable N have been of two types:-(i) chemical extractions designed to remove organic fractions of N which correlate well with that fraction which becomes available and; (ii) incubation procedures that simulate the release of N from soils. The latter, which consider the biological and environmental variables have been more

successful.

There are many problems associated with estimating the N supplying power of soils in the laboratory(Bremner,1965; Robinson,1975). Not the least is the empirical nature of the various methods, which provide relative rather than absolute values for nitrogen supplying power(Stanford,1977). Through the work of Stanford and co-workers, however, a less empirical expression has been provided(Campbell,1978). Stanford and Smith(1972) defined the potentially mineralizable N, (No) as the total quantity of soil organic N that is susceptible to mineralization at time zero according to first order kinetics. Another value, k is defined as the mineralization rate constant. The approach is promising because it conforms to some of our basic tenets, for example, that nitrogen mineralization is related to an 'active' nitrogen fraction and not to total soil nitrogen (Campbell et al.,1981).Tabatabai and Al-Khafaji(1980) also consider that the basic procedure involved, i.e. leaching and incubation - seems to simulate the removal of mineral N and S by plants and leaching processes under field conditions.

With the exception of a recent report by Tabatabai and Al-Khafaji(1980) however, there appears to be no other reports on the use of this approach to assess the S supplying power of soils.

It has been assumed that the relative rates of mineralization of these two elements would be similar,i.e. N

and S are mineralized in approximately the same ratio as they occur in soil organic matter(Walker, 1957; White, 1959). Data summarised by Biederbeck(1972) and Tabatabai and Al-Khafaji(1980) however failed to show any consistency in the relationship between mineralization of the two elements. Most of the data were obtained mainly using continuous incubation procedures. The reliability of results derived from extended incubations in such static, closed systems is questionable(Stanford, 1982).

Amounts of organic forms of C,N and S are highly correlated in most soils. Results from comparison of paired virgin and cultivated soils however showed C and N to have accumulated and mineralized at similar rates, whereas S accumulated and mineralized at slower rates(Swift, 1976). An explanation for this divergent behaviour between C and N on one hand and S on the other has recently been proposed in a concept by McGill and Cole(1981). Briefly, the concept proposed that mechanisms stabilizing C, N, S and P are not necessarily common to all four elements, and pathways of mobilization are specific to the organic molecule being hydrolysed or oxidized. A dichotomous system exists in which N and part of the S are considered to be stabilized as a result of direct association with C(N and C-bonded S) and to be mineralized as a result of C oxidation to provide energy(classical biological mineralization). Organic P exists mostly as esters and is stabilized by adsorption and precipitation with soil components. Organic P and ester

forms of S are considered to be mineralized in response to the need for the element. They termed this process biochemical mineralization, because it operates largely outside the cell and is controlled by the need for the element released.

The objectives of this study therefore are:

1. to determine the relationship between N and S mineralization rates using two methods of incubation, i.e continuous incubation in pots, and the incubation and leaching technique of Stanford and Smith(1972).
2. to determine the potentially mineralizable N and S for a broad range of central and southern Alberta soils using the technique of Stanford and Smith(1972) as modified by Smith et al.(1980).
3. to study the changes in the distribution of soil organic N and soil organic S fractions brought about by long-term natural mineralization processes. To achieve this, virgin and adjacent cultivated soils of the Chernozemic order and fallow and non-fallow soils of the Luvisolic order will be compared. An attempt will be made to assess the effectiveness of McGill and Cole's concept in predicting some of these changes.

II. LITERATURE REVIEW

Although N and S mineralization have similarities, they are not parellel metabolic processes(Kowalenko and Lowe,1975). Biederbeck(1978), after reviewing results from experiments comparing N and S mineralization, concluded that it would appear that in contrast to the behaviour of N, the rate and extent of release of plant available S is not closely governed by major soil characteristics such as organic C,N and S content. To explain these behavioural differences McGill and Cole(1981), proposed a dual mechanism for S but not N mineralization from soil organic matter. Finally, among the important plant nutrients released from soil organic matter, the behaviour of S is thought to be intermediate between those of N and P(McGill and Cole, 1981).

Therefore, this literature review will be discussed in three parts:

1. N availability, its estimation and factors affecting its estimation
2. S availability, its estimation and associated factors.
3. Relationship between N and S mineralization.

A. NITROGEN AVAILABILITY AND ITS ESTIMATION

There does not appear to be any universally accepted method for testing soils for available N. This is a reflection in part, on the fact that 97-99% of the N in soils is present in very complex organic compounds that are

not available to plants(Dahnke and Vasey,1973). Generally, only about 25-50% of the total N in hydrolysates of surface soils has been identified,i.e. 20 to 40% as amino acid-N and 5 to 10% as amino sugar-N. A large proportion of N (usually 20 to 30%) has also been recovered as NH_3. Some of the NH_3 is of inorganic origin; part comes from amino sugars and amino acid amides, asparagine and glutamine(Stevenson, 1982).

Organic N slowly becomes available to plants through microbial decomposition of the organic matter. There is some difference of opinion as to how many components (from a stability view point) there are; however the general consensus is that there are at least three and probably four components. In order of decreasing ease of decomposition these are fresh residues, biomass material, microbial metabolites and cell wall constituents adsorbed to colloids, and the old very stable humus. It is primarily the fresh residues and the biomass which give rise to most of the N released to plants(Campbell,1978).

The problem of developing a test for available soil N is further complicated by the following factors:

1. the rate at which microorganisms decompose soil organic matter is dependent on temperature, moisture, aeration, type of organic matter, pH and other factors
2. the main form of available N, NO_3^--N is subject to leaching, denitrification and immobilization by soil microorganisms.

Biological N Availability Indexes

The following procedures have been used by various workers to assess N availability indexes biologically.

1. Aerobic Incubation
2. Anaerobic Incubation
3. Microbiological Assay
4. Measurement of CO_2 production

1a. Aerobic Incubation Procedures.

Numerous aerobic incubation procedures have been used. The main differences among them are length of incubation period, temperature, moisture content and use of amendments. Attempts to agree on optimum conditions have been largely unsuccessful because, as pointed by Mahendrappa et al.(1966), nitrifying bacteria found in a particular soil are the result of natural selection and adjustment to the climate. Similar observations were made by Russell et al.(1925) with respect to temperature and moisture.

In the simplest type of incubation experiment the analysis for mineral N is performed only twice; at the beginning and at the end of the incubation period. The difference between these two determinations divided by the length of the incubation period gives the average rate of the mineralization during the experiment. The assumption here is that the rate of mineralization remains constant more or less throughout the incubation. This assumption is however not valid(Harmsen and Van Schreven, 1955). Apart from the well known depression of nitrogen mineralization

during the first weeks of incubation in all soils rich in undecomposed organic matter with a high C:N ratio, the rate of mineralization of N in soils has been found to be dependent of time.

By repeated analysis during incubation, the rate of nitrogen mineralization has been shown to decrease with time. Various reasons have been proposed to explain this gradual decrease in mineralization. Allison and Sterling(1949) proposed that it might be due primarily to increasing acidity caused by nitric acid produced during incubation, and Acharya and Jain(1954) supposed that water soluble toxins may be formed during incubation which ultimately suppressed the mineralization. Contrary to the view of Allison and Sterling, Acharya and Jain found no perceptible drop in pH during nitrification in the soil samples they worked with.

In practically all cases, this slowing down and ultimate cessation of mineralization has been overcome by leaching the samples with water and allowing them to incubate again. Mineralization under such conditions seemed to go on indefinitely(Harmsen and Van Shreven,1955). The leaching and incubation technique has been subjected to many modifications. Some changes made to the original procedure developed by Stanford and Hanway(1953) by later workers notably Stanford and Smith(1972), are the use of 0.01M $CaCl_2$ solution instead of water and the replacement of vermiculite with sand for mixing the soil samples. The use of $CaCl_2$ for

leaching removes both NO_3^--N and NH_4^+-N especially under conditions where ammonium produced during incubation does not nitrify completely. It also preserves physical stability by preventing dispersion. Vermiculite was originally used to facilitate moisture control due to its high water holding capacity and to minimize compaction of soils when suction is applied to remove excess liquid(Stanford and Hanway,1953). Vermiculite however, is known to fix NH_4^+-N(Bremner,1965); thus its replacement with sand will rectify this drawback. Synghal(1958) in this department had however observed that the leaching and incubation technique gave large variations in replicates as compared to nitrate accumulation determined by incubations in jars. He attributed these variations to different degrees of compaction caused by strong suction used while leaching the soils prior to incubation. The leaching and incubation technique has the advantage of providing automatically an integration of the effects of substrate amount and composition that affect the natural process in the field(Campbell,1978). It seems to simulate the removal of mineral N and S by plants and leaching processes in soils under field conditions (Tabatabai and Al-Khafaji,1980). It has been used in recent times by many workers to find that portion of soil organic N which is susceptible to mineralization. The approach is promising since it seems to conform to some of our basic tenets, for example, that nitrogen mineralization is related to an active fraction and not to total soil N (Campbell et

al.,1981).

Stanford and Smith(1972) first defined the N mineralization potential (No) of a soil to be the quantity of soil organic N susceptible to mineralization according to first order kinetics, i.e. $-dN/dt=kN$. To estimate No, the integral of the above expression $\ln(No-Nt)=\ln No-kt$ was used by Stanford and Smith(1972). (Nt denotes cumulative N mineralized over time t; and k is the rate constant per time e.g. one week). The value of No resulting in the best fit from the regression of ln(No-Nt) on t was taken as an estimate of N mineralization potential. The slope of the regression is k(Stanford and Smith,1972).

Stanford and Smith's procedure has been tested *in situ* (Smith et al.,1977; Herlihy,1979), for short periods in the greenhouse(Stanford et al.,1973), and for crop growth under field conditions(Stanford et al.,1977; Oyanedel and Rodriguez,1977). Although these tests were carried out in different countries with differing climates, the relationship between the N mineralization rate constant (k) and absolute temperature(T) developed in the U.S.A by Stanford et al.(1973) has been shown to have wide applicability(Campbell et al.,1981).

Bremner(1965a) in a review of N availability indexes listed a number of criticisms and defects of the leaching and incubation technique, most of which were corrected in later work. The suggestion, however, by Bremner(1965a) that leaching will remove soluble organic-N compounds which are

readily mineralizable, was later confirmed by Legg et al.(1971), Broadbent and Nakashima,(1971) and Smith et al.(1980). Leaching of readily mineralizable substrate should lower subsequent values of N mineralisation. Furthermore the amount of mineral N measured becomes highly dependent on the number of leachings carried out during an overall mineralization study(Smith et al.,1980). Smith et al.(1980) further showed that leaching of potentially mineralizable substrate influenced values of both No and k. There were significant differences in predicted values of No and k using values of total N leached rather than using values of mineral N which has been the usual approach. They further recommended the use of a non linear regression technique for determining the 'best fit' of experimental data to a first order kinetic equation,i.e.$-dN/dt=kN$. It is more precise, less ambiguous and in many respects simpler than the traditional linear regression approach proposed by Stanford and Smith(1972). This assertion is substantiated by the findings of Talpaz et al.(1981). Analysis of Stanford and Smith's(1972) data by Talpaz et al.(1981) using non linear regression techniques gave lower estimates for No and lower standard errors than those obtained by Stanford and Smith(1972).

1b.Limitations of the Aerobic Incubation Method.

Incubated soil samples are kept under entirely artificial conditions in efforts to approach as much as

possible the conditions ideal for mineralization of organic substances. Such incubation experiments do not simulate field conditions. Still it is not advisable intentionally to make the incubation conditions less favourable for mineralization, because only by creating optimal conditions can the method be standardised (Harmsen and Van Schreven, 1955).

Bremner(1965a) stated that results obtained by incubation methods for comparisons of mineralizable-N in soils are pointless unless methods of sampling, drying, grinding, sieving, storing and incubating the soils are rigourously standardised. He proposed that samples for estimation of mineralizable N should be taken in the winter or during the spring.

Most workers have apparently taken surface samples in the spring, then air dried and stored the samples for some time before analysis. Though this procedure is convenient, it has been found that air drying of soil samples increases the values obtained for mineral-N. Therefore, the present trend is toward storage of field moist soil samples at cool temperatures e.g. 4°C, whilst waiting for analysis.

Soil samples have often been mixed with sand before incubating(Keeney and Bremner, 1966; Stanford and Smith, 1972). According to Robinson(1975), this convenience will be generally acceptable provided it is not used to convert a soil sample that is naturally waterlogged in the field for all or part of a crop season into a well aerated soil for

incubation. Even this may be justified however, where such a soil is pot tested under greenhouse conditions, provided it is amended in exactly the same manner for this purpose. Harmsen and Van Schreven(1955), had earlier questioned this treatment on the grounds that the soils will be completely changed, so that observed results will no longer correspond with the characteristics of the original samples.

In addition to physical amendment of soil samples with sand, chemical and biological amendments have often been used. Nutrient status of laboratory or greenhouse samples should not be further removed from the natural state than can be avoided. If however, deficiency or imbalance of nutrients is likely to limit the test crop growth under greenhouse conditions, e.g. a severe P deficiency, this should be eliminated in pot soils by chemical addition and the same treatment, should be applied to the laboratory test soil(Robinson,1975).

The amendment of soils for incubation with, e.g. addition of minus-N nutrient solution - a practice normally used in the leaching and incubation technique - may substantially improve mineralization of N (Robinson,1975). Base exchange status has been shown to be associated with nitrogen supply to the crop(Conforth and Walmsley,1971; Walmsley et al.,1971; Walmsley and Baynes,1974; Cornforth,1974). If soil pH limits nitrogen mineralization under natural conditions and this is not corrected for the test crop, there should be no modification of the soil

sample for laboratory incubation. Introduced differences such as these between the chemical fertility of the index sample and the cropped soil may substantially distort data. (Robinson, 1975).

2.Anaerobic Incubation Procedure.

Incubation of soils under anaerobic(waterlogged) conditions and measurement of NH_4^+-N released has attracted attention because of its simplicity. A close relationship between the amount of NH_4^+-N produced by anaerobic incubation and the amount of NH_4^+-N , NO_3^--N and NO_2^--N produced on incubation of a soil under aerobic incubation was reported by Waring and Bremner(1964). Close correlations between the two methods are not universal, however, and in reviewing the subject Stanford(1982) concluded that soil N availabilty provided by anaerobic incubation procedures may be uniquely suited to estimating the N supplying abilities of flooded rice soils.

The anaerobic incubation procedure has the advantages that (i) no amendments, such as sand need to be added as is done in some aerobic incubation experiments; and, (ii) it is not necessary to aerate. It would have the disadvantage that any NO_3^--N initially present in the soil may be lost by denitrification(Dahnke and Vasey,1973).

3.Microbiological Assay Methods.

These methods generally involve measurement of microbial activities such as growth or pigment production following incubation with a nitrogen-free nutrient medium and a microbial culture.

Tchan(1959), criticised these procedures as unsatisfactory for the following reasons:

1. Unsuitable reaction (pH) of the assay system
2. Addition of organic matter other than that of the soil sample.
3. Side effects resulting from sterilization of the soil sample
4. The unsuitability of the test organisms used.

Though Tchan et al.(1961), proposed an algal technique to rectify the above criticisms, in general the microbiological methods have received little attention (Bremner,1965a).

4.Methods of CO_2 Production.

These methods have been described as indirect incubation procedures(Harmsen and Van Schreven,1955). They are based on the assumption that if a soil sample is mixed with an excess of free readily decomposable organic material, the amount of CO_2 produced will depend upon the amount of mineral-N originally in the sample and the amount of N mineralized during the incubation. The validity of this assumption is questionable, because N may not be the only nutrient which limits mineralization of organic carbon when soils are incubated with nitrogen-free energy-rich materials, and treatment of soils with such materials promotes fixation of atmospheric N_2 by soil organisms (Bremner,1965). In spite of these limitations Cornfield(1961), found that the amount of CO_2 produced when soil samples treated with 1% cellulose were incubated for

three weeks, was highly correlated with the total amount of mineral-N present in unamemded soil samples incubated for the same period and he obtained evidence that N was the only nutrient limiting microbial mineralization of organic C in the soils tested. Earlier work by Synghal(1958) in this department showed a close relationship between CO_2 evolution and NO_3 accumulation in some soils but not in others.

Robinson(1975), criticised biological methods which measure CO_2 evolved, microbial growth or soluble carbohydrates. Such methods are one step removed from the true end point of the system which is mineral-N, and may permit the inadvertant introduction of uncontrolled factors. Whether the supply of energy does, or does not exert a dominant or controlling effect within the natural system and is well correlated with mineral-N or crop parameters, it is the mineral-N which is directly involved in crop production. Furthermore the quantity of the mineral-N after standard incubation is the result of the balance between mineralization and immobilzation in a soil. This balance may be altered by a one sided chemical amendment of laboratory or crop- test soil samples(Robinson,1975).

Chemical N Availability Indexes

Incubation methods of determining the nitrogen mineralization capacity of soils are time consuming and laborious. Chemical methods for obtaining a nitrogen availability index for a given soil are attractive because

they are usually rapid, precise, and more convenient than incubation or field methods. The principal criticism of these methods is that no extraction agent is likely to simulate the action of soil microorgnisms in releasing N over a period of several months(Bremner,1965a; Broadbent,1981).

Of the various chemical indices proposed, few have been shown to correlate well with N released by biological methods for a broad range of soils, and none has been put to general, practical use in assessing the nitrogen supplying capacities of soils (Stanford and Smith,1978). The possible utility of any chemical index for a broad range of soils depends on the degree to which it correlates with reliable biological measurements of soil N availability, e.g. N uptake, crop yield, or mineralization of N(Robinson,1975; Stanford,1982). Most of the proposed methods have involved measuring NH_4^+-N, total organic N, total organic matter, and total organic carbon extracted by acid, alkaline reagents and oxidants (Bremner,1965; Stanford,1982). Milder extraction methods are boiling in water(Keeney and Bremner,1966), boiling in 0.01M $CaCl_2$(Stanford,1968) and autoclaving in 0.01M $CaCl_2$(Stanford and DeMar,1970).

Methods involving determination of total N, organic matter and organic carbon appear to have limited value(Harmsen and Van Schreven,1955; Allison,1956). Though there is a general relationship between total soil N and the amount of available N released during a growing season

(Campbell,1978), there is some controversy regarding the usefulness of this method because of the many factors that affect the release of available N from soil organic matter (Vlassak,1970; Allison,1973). It has been demonstrated repeatedly that total soil N does not constitute a reliable index of soil N availabilty for a broad range of soils(Stanford and Smith,1978; Stanford,1982).

One method which appears to have aroused much interest is the alkaline permanganate method proposed originally by Truog(1954). Results with this method are however not satisfactory. Synghal(1958) found no significant correlations between available nitrogen and crop yields in the field with this method. Bajaj et al.(1967), compared eight methods for estimating available N, using rice and wheat as test crops on different soils, and found the alkaline permanganate method to give the best correlation with yield. Stanford(1978) evaluated ammonium release by alkaline permanganate as an index of soil N availabilty, and concluded that it was less reliable and precise than the acid permanganate extraction method. More recently, Sarawat and Burford(1982), also observed that nitrate and nitrite would not be included in the alkaline permanganate method. It has an oxidising action and therefore would not reduce nitrate-N to ammonium-N. A simple modification involving the use of Devarda's alloy allows the inclusion of nitrate and nitrite(Sarawat and Burford,1982).

Fox and Piekieleck(1978), compared eight methods for obtaining a nitrogen availability index on soils in Pennsylvania. Of the methods tested, amounts of N extracted with boiling 0.01M $CaCl_2$ and with 0.01M $NaHCO_3$ were the only two which correlated at the 1% level of significance with the N supplying capacity of eight soils in two seasons. Autoclave extractable NH_4^+-N; i.e. the amount of NH_4^+-N released in 0.01M $CaCl_2$ and total soil N were correlated at the 5% level. Soil NO_3^--N, H_2SO_4 and KCl extractable- N were not significantly correlated with N availability in the field.

While calibrated for a particular climatic region and a reasonably narrow range of soils, chemical extraction procedures can be useful in assessing potential N availability, but it is important to consider past history of the soil and rainfall patterns when interpreting results of such tests(Broadbent,1981).

Initial Inorganic N Tests.

The potential of a soil to mineralize N as measured by N availability indexes is fairly constant from year to year, making it unnecessary to make that type of determination each year. It is still necessary, however, to take into consideration the initial amount of available N in the rooting zone at planting time. Both biological and chemical tests have been used to assess initial inorganic N(Dahnke and Vasey,1973), but the latter tests have received more

attention than the former.

The biological methods differ from the chemical methods in the following ways: -(i)the amount of biological growth is measured rather than directly measuring inorganic N (i) it is not normally possible to determine if NO_3^--N or NH_4^+-N is present using biological methods.

Nitrate-N is readily used by higher plants and also is the form that usually accumulates in normal agricultural soils. NO_3^--N at seeding time is the method used in the Canadian prairies to predict crop response to added fertilizer N. Generally, initial NO_3^--N values are useful in predicting crop growth only in arid areas where the NO_3^--N is not leached out of the soil profile by precipitation(Fox and Piekielek,1978). In the Canadian prairies,losses of mineral N by leaching and denitrification are considered minimal(Campbell,1978). Thus most of the mineral N found in soil at planting time will be available to the crop throughout its growth. Soper et al.(1971) showed that a very close correlation existed between barley uptake of N and the amount of NO_3^--N to a depth of 61 cm in a soil sampled at time of seeding.

Sampling to appropriate depths to obtain most of the NO_3^--N in soil profiles is one of the several factors which affect the usefulness of the NO_3^- test and this may not be the same on all soils(Campbell, 1978). This test is suitable for annual cropping as practised in western Canada; however, with continuous cropping(eg. forage crop), it is of little

use because there is little mineral N in the soil at any time of the year(Campbell,1978).

Where rainfall is high, one or more of the other methods used to assess N availability has been used singly or in combination with initial mineral N. The use of N availability indexes in addition to initial NO_3^--N usually improves correlation with N uptake by crops(Dahnke and Vasey,1973). Poor correlations of initial mineral N with N uptake by crops have been reported by Ryan et al.(1971) and Fox and Piekielek(1978b) in Kentucky and Pennsylvania respectively. This was attributed to the high amounts of rainfall in those areas.

Factors Affecting N Mineralization

Oxidation of organic substrates in soils and subsequent mineralization of nitrogen is catalysed by a wide variety of heterotrophic microorganisms whose activity is governed by the chemical composition of the substrate and the physical and chemical characteristics of their environment. Temperature, oxygen tension, moisture, pH, inorganic nutrients, some cofactors and the C:N ratio of the substrate are the main environmental influences (Alexander, 1977; Campbell, 1978) The effect of temperature on soil microorganisms varies in response either to moisture change or initial moisture content or both (Campbell and Biederbeck,1976). Significant interactions have been observed between moisture and temperature effects on net N

mineralization (Cassman and Munns,1980; Sarathchandra and Upsdell,1981).

During a particular season there is a marked variation in temperature and rate of N mineralization (Robinson, 1975). There are differences between successive seasons in the quantities of mineralized N made available to a crop on the same soil in response to total rainfall and its distribution, and to length and intensity of dry and wet periods in the pre crop season. When a soil is kept under fairly constant conditions its biological activity and net mineralization declines to a low level. If however, the current state is interrupted by unfavourable conditions; e.g. drought or frost, and thereafter re-established, a stimulation of biological activity is often found. Consequently, such factors as drying and wetting, freezing and thawing, ploughing, partial sterilization(e.g. by chemical sprays), often cause a subsequent flush; the magnitude of which is a function of the amount of disruption (Campbell, 1978).

The heterogeneity of the microflora responsible for nitrogen mineralization is a critical factor in determining the influence of environmental factors on N transformations. Because aerobic and anaerobic, acid sensitve and acid resistant, and spore forming and non-spore forming microorganisms function in the degradation of nitrogenous materials, at least some segment of the population is active regardless of the peculiarities of the habitat as long as

microbial proliferation is possible. Consequently, mineralization is never eliminated in arable land, but the rate is markedly affected by environment(Alexander,1977).

The role of microfauna in organic matter transformations has received some attention in recent years. Johannes(1968), reported that mineralization of N and P from organic matter in aquatic systems is strongly dependent on 'grazing' of the bacterial populations by microfauna. Woods et al.(1982), investigated this phenomenon in microcosms, and found as the microbial biomass increased, it assimilated N from the soil. Later, only if this bacterial biomass decreased was N remineralised. 'Grazing' by amoebae always reduced bacterial biomass, increased respiration, and increased nitrogen mineralization. Death or reduction in microbial biomass has been found to lead to increases in N mineralization(Monreal and McGill,1981) and potentially mineralizable N estimates(Carter and Rennie,1982). 'Grazing' by nematodes reduced the bacterial population and only increased respiration when nematode populations themselves declined from peak values. Thus soil N mineralization should not be viewed as strictly bacterial or fungal. Microfauna may play an important role in soil N mineralization and the mechanism for this role is more likely to be through direct excretion by the 'grazers' than through indirect physiological effects on the bacteria(Woods et al.,1982).

Previous Cropping History.

The effects of previous crops on correlations between mineralizable-N, and N uptake by a test crop are reported for grass, legume and corn(Smith,1966); for a crop following cotton, rice, lespedeza or soybean crops (Sims and Blackman,1967), for crops following grass/clover and grass leys(Gasser and Mitchell,1968;Gasser,1969b; Clement and Black,1969), and for corn following corn or alfalfa(Spencer et al.,1966).

In any quantitative evaluation of a soil N availability index, previous cropping history or the different stages of a crop rotation have to be considered when grouping units (Robinson,1975).

Effect of Cultivation.

Cultivation enhances net mineralization of nitrogen in soil. In spring, soil that had been direct drilled to winter cereals, contained roughly 30kg ha^{-1} less mineral N than soil that had received conventional tillage (Powlson,1980), and during a growing season at Swift Current, net N mineralized under fallow on a Brown Chernozem was 103 kg ha^{-1} while under crop it was 52 kg ha^{-1}(Campbell et al.,1980). Incorporation of dead roots and plant residues coupled with better aeration of the soil and breakdown of complex substrates into lower molecular weight compounds,

creates favourable conditions for microbial activity when fields are cultivated. While this could explain Powlson's observation in England, a more appropriate explanation for the observation at Swift Current would be the reduction in quantity or death of microbial biomass. Voroney et al.(1981), showed that the level of microbial biomass C and N in the Ap horizon of a soil in a crop-summer fallow rotation was approximately 30% lower than in the Ah horizon of a native prairie grassland in Saskatchewan.

It has been suggested by Jenkinson(1981) that the greater the initial nitrogen content, the greater the fall when cultivated. Powlson(1980), however found a higher difference in mineralized N between a cultivated soil and uncultivated soil at a site with less total organic matter than at a site with a higher organic matter content. He attributed this observation to the higher content of more recently added material from plant roots at the site with less organic matter content. This more marked effect of cultivation may indicate that cultivation accelerates the decomposition of fresh organic matter more than those of the older, more stable parts of the soil organic matter (Powlson,1980). This is consistent with the view that fresh residues are the most easily decomposable components of soil organic matter (Campbell,1978) and results of laboratory experiments on grinding as reported by Craswell and Waring(1972). Craswell and Waring(1972), found that despite a large decrease in total organic matter content, the

cultivated soils still showed large proportional increases in decomposition rates due to grinding. These large increases suggest that field tillage exposes organic matter for decomposition.

Increases in mineralization caused by cultivation in the old arable soils used by Powlson were however much less than those found by Dowdell and Connell(1975), who used soils of higher organic matter content. Thus Powlson(1980), concluded that the effect of cultivation on mineralization of soil N varies considerably between soils, probably dependent on the organic matter of the soil, particularly the fresh organic matter content.

Paired virgin and cultivated soils have often been used in attempts to characterise the readily decomposable fraction of soil organic matter, since chemical fractionation has not been highly successful for this purpose. Incubation studies by various workers have however shown that cultivation causes not only a decline in the total organic matter but also in the proportion which mineralizes during incubation(Craswell and Waring,1972).

B. SULPHUR AVAILABILITY AND ITS ESTIMATION

Like phosphorus, sulphur is a major nutrient for plants and animals, and a relatively minor constituent of soils(Allaway and Thompson,1966). It also exists in unavailable states, so that responses to S-containing fertilizers are not uncommon(Alexander,1977). The major

reserve of the element in soil is the organic fraction.

It is generally accepted that plant-available sulphur in the soil includes soluble inorganic sulphate, the adsorbed sulphate and part of the organic S which is mineralized over the growing season. While it is generally agreed that soluble and adsorbed sulphate in the soil comprise the main source of sulphur for plant uptake, there is less agreement on the methods of extraction(Metson,1979). These two sulphate fractions are similar in size to the available S pool determined by isotopic dilution techniques and can be considered to be the soil's instantaneous supply of available S (Probert and Jones,1977). The adsorbed sulphate fraction may however comprise sulphate retained with a range of energies so that it is not all equally available (Metson,1979).

As a general principle, for any given nutrient in any particular crop, two approaches are available for assessing the adequacy of plant nutrition, namely soil analysis and plant analysis. For some elements one method or the other is to be preferred, but this does not apply to sulphur (Metson,1979). Assessment of available sulphur status of soils is complicated by the multiciplicity of sources of S and the varying proportions from each source. These include soil S, S in precipitation and irrigation water and S in fertilizers and pesticides(Reisenauer et al,1973).

Numerous procedures have been proposed for evaluating the S status of soils. These have included extraction with

water, extraction with various salts and acids, S release upon incubation, microbial growth, and plant growth and composition including "A" value (isotopically exchangeable S) determinations. The S removed by these extractants tends to fall into the following groups:(i) readily soluble sulphate (ii) readily soluble and portions of adsorbed sulphate (iii) readily soluble and portions of adsorbed sulphate and portions of organic matter(Reisenauer et al.,1973).

Endeavours to relate plant growth to total or organic soil sulphur have been largely unsuccessful, but some useful relationships with the extractable soil-S fractions have been found. It would appear that the choice of extractants selected may be influenced by the the amount and kind of available sulphate present in the soils concerned (Metson,1979). Thus the use of extractants incorporating the weakly adsorbed Cl- anion seems to have been favoured in areas of low rainfall where the soils contain predominantly 2:1 (micaceous) clays and have low levels of largely water soluble available sulphate-S (Williams and Steinbergs, 1959;1964; Chao,1964; Roberts and Kochler,1968; Carson et al.,1972; Tabatabai and Bremner,1972; Walker and Doornenbal,1972; Westerman,1974; Bettany et al., 1973;1979). Water-soluble sulphate has also been used by some workers, although not always successfully(Williams and Steinbergs, 1959; Fox et al., 1964; Westerman,1974). The fact that water-soluble sulphate often closely approximates

chloride-extractable sulphate in many low rainfall areas with soils containing predominantly 2:1 clays, suggests that little, if any adsorbed sulphate is present(Metson,1979).

In regions of high rainfall where soils are more weathered, and particularly where they contain sesquioxides or allophanic or kaolinitic clays, the available or adsorbed sulphate is not only present in greater amounts but is strongly held by the soil colloids(Metson,1979). Consequently, methods of extraction generally employ the more strongly (specifically) adsorbed phosphate anion (Ensminger,1954; Bardsley and Lancaster,1960; Fox et al.,1964; Barrow,1967; Bromfield,1972; Hoeft et al.,1973; Probert,1976; Blakemore et al.,1977; Probert and Jones,1977; Tsuji and Goh,1979). In Alberta, results from work of Sorenson(1965) showed that sulphate amounts extracted with KH_2PO_4(500 p.p.m P) were generally higher than amounts extracted with water. Sulphate amounts extracted with 0.001N HCl were however of the same magnitude as those extracted with KH_2PO_4. Higher amounts of sulphate extractable by $Ca(H_2PO_4)_2$ than LiCl were ascribed to the presence of adsorbed sulphate in Brazilian soils(Neptune et al.,1975), while identical amounts of extractable sulphate found in extracts of $Ca(H_2PO_4)_2$ and LiCl in Iowa soils were attributed to the absence of adsorbed sulphate in these soils(Tabatabai and Bremner, 1972).

The basic weakness of the methods used to measure extractable S, is that they are correlated with S uptake

only on S deficient soils and fail to provide an estimate of the reserve forms of sulphur which is required for an assessment of the long-term S supply in non-deficient soils(Freney et al.,1962; Rehm and Caldwell,1968). Another important source of S for plant nutrition is extractable S in the subsoil. Probert and Jones(1977), therefore proposed that, in predicting the available S status of soils, it is necessary to consider the whole soil profile. This is yet to receive due attention.

Availability of Organic S

A large proportion of soil sulphur may be organically bound (Anderson,1975), especially in non-calcareous soils of the humid regions(Scott and Anderson,1976). It is however possible that unlike phosphorus, it may exist predominantly as an integral part of the soil organic matter, and consequently be resistant to extraction and degradation (Scott and Anderson,1976). Although soil organic phosphorus is thought to be exclusively in the form of phosphate, not all organic sulphur is sulphate (Anderson,1975).

There are two fractions (not extractable as such from soils) that together account for most of the soil organic sulphur; the HI-reducible fraction(the reductant is actually a mixture of hydriodic, formic and hypophophorous acids) and the 'Raney-nickel reducible' fraction. The former is generally considered to be mainly sulfate esters which is predominantly O-bonded sulphur(C-O-S), with possibly some

sulfamates(C-N-S), and the latter group includes the sulfur-containing amino acids and the sulfonates in which S is directly bonded to carbon. These are referred to as C-bonded S(Fitzgerald,1978).

It is generally accepted that plants take up their sulphur as inorganic sulphate and the availability of soil organic sulphur thus depends upon its mineralization (Williams,1967). Freney et al.(1975), found that plants were able to obtain their sulphate from both ester-sulphate and C-bonded S in soils, with the latter fraction contributing the greater proportion.

The quantity and nature of the labile S in soils is variable and frequently the inorganic sulphate pool is large enough that contributions from mineralization of organic sulphur can be neglected. In situations where soils contain low amounts of inorganic sulphate, mineralizable S may be critical in preventing sulphur deficiency in plants(Bettany et al.,1974; Lee and Speir,1979). Lee and Speir(1979), found that more S was taken up by plants than could be accounted for by the fall in adsorbed sulphate levels during a greenhouse trial. This S is believed to have been mineralized during plant growth (Cowling and Jones,1970; Fitzgerald,1976).

Recent results from studies on the availability of soil organic S tend to suggest that it is extremely difficult to devise a satisfactory method for predicting the S requirements of plants. To be useful, a soil test for S

availability must provide a reasonable estimate of that part of the soil organic S which is mineralized during a growing season. Under field conditions, complications may arise from uptake of S from different subsoil horizons(Goh et al.,1977; Gregg et al., 1977; Probert and Jones,1977), its movement as affected by adsorption and/or leaching in the soil profile, and the unpredictable rates of mineralization and immobilization of soil organic S which are determined largely by environmental conditions (Tsuji and Goh,1979).

The development of diagnostic methods for estimating the S supplying power of soils has generally followed the approaches used for elements such as N and P. These have involved attempts to extract the labile fraction of organic S by various chemicals, soil incubation and microbiological assays. Defects, limitations of and criticisms levelled against these methods when used to estimate N availability indexes would apply if they are used to estimate S availability indexes.

Chemical S Availabilty Indexes

Total S content of soil is not related to the mineralizable or plant available S(Ensminger and Freney,1966). Thus special methods have been devised in an attempt to extract the labile fraction of soil organic S. Although methods proposed for extraction and estimation of labile soil S are generally based on arbitrary assumptions, some of these attempts have proven rather useful

(Biederbeck,1978).

Two of the methods proposed for extracting available S are of special interest, because they measure also a portion of the more labile S, and hence possibly more available S, in the soil organic matter. These are the methods of Williams and Steinbergs(1954), for heat-soluble S(S extracted with NaCl and drying in an oven at 100°C), and the bicarbonate method of Kilmer and Nearpass(1960), using $NaHCO_3$ at pH 8.5. As would be expected, these methods, more especially the bicarbonate one, extract more S than the phosphate, acetate(Ensminger,1954; Fox et al.,1964), or chloride extractants(Bardsley and Kilmer,1963). They have however not come into general use perhaps because of difficulties in interpreting the results (Metson,1979).

Biological S Availability Indexes

Incubation procedures of the type commonly used for assessing the availability of N in soils appear to offer little promise for estimating the S availability status of soils, because little sulphate is formed especially in the absence of plants(Nicolson,1970), and its precise measurement is difficult(Reisenauer et al.,1973; McLaren and Swift, 1977). Thus understanding of S distribution in soil and its role in plant nutrition has been impeded in the past by lack of sensitive analytical methods(Metson,1979). In spite of the above statements most of the information on the role of mineralizable S in plant nutrition and relationship

between N and S mineralization have been obtained through aerobic incubation procedures. Recently, Tabatabai and Al-Khafaji(1980), used the leaching and incubation technique to assess mineralization rates of S in Iowa soils. Contrary to what most workers have reported from other incubation studies, mineralization rates were higher for organic S than organic N in their study.

Microbiological assay using *Aspergillus niger* have been examined(Ensminger and Freney, 1966). This fungus can obtain amounts of S from soils similar to those extracted with phosphate solutions. It has however not received much attention in recent years probably because of the perceived unsuitability of microbes as test organisms as pointed out by Tchan(1959).

C-bonded S, Ester Sulphate and S mineralization

Reports on the relative contribution of the two recognised forms of organic S to S mineralization are conflicting. The hydrolytic cleavage of the ester bond may not be the rate limiting step in the mineralization process(Speir and Ross,1978). This is consistent with the suggestion by Somiento(1972), that the rate of mineralization of C-bonded S might be the rate limiting factor in the supply of S to plants from soils that have low levels of available sulphur. Furthermore, Freney et al.(1975), found that plants were able to obtain their sulphate from both ester sulphate and C-bonded S in soils,

but greater contribution came from the latter fraction. In an incubation study however, Freney et al.(1975), observed that ^{35}S labelled fertilizer was incorporated into both HI-reducible and C-bonded S fractions, but the former fraction was more highly labelled and it was from this fraction that plants later derived all of the labelled-S taken up. Somiento (1972), on the contrary, had reported that though added sulphate was incorporated into both forms of organic S, mineralization came from the C-bonded S fraction, while the ester-sulphate fraction remained constant. The rate of mineralization appeared to be independent of the rate of incorporation(Somiento,1972).

Comparison of S distribution in pasture and arable soils showed that the greater proportion of mineralized S was due to the C-bonded S fraction(McLaren and Swift,1977). Despite this observation, these workers suggested that ester-S is more important in the short term mineralization, whereas C-bonded S is more important in the long run and passes through an HI-reducible form prior to the release of inorganic sulphate. Freney et al.(1975), observed marked increases in the HI-reducible fraction of unlabelled S which they suggested indicated the conversion of C-bonded S to HI-reducible S during incubation. HI-reducible S fraction has been observed to decrease during plant growth, but no close correlation has been observed between this fraction and plant S uptake(Freney et al.,1975; Tsuji and Goh,1979). In contrast, Lee and Speir(1979), found that uptake of S

from organic sources was significantly correlated with ester-S and organic S, but not with C-bonded S. In addition, their results indicated that C-bonded S is less important in short term mineralization in consonance with the suggestion made by McLaren and Swift(1977). Bettany et al.(1979), however felt that in view of the observations showing that both fractions contribute significantly to S mineralization, separation of organic S into sulphate ester and C-bonded S is neither selective nor sensitive enough for any meaningful interpretation.

Role of Sulfohydrolases in S mineralization.

Liberation of inorganic sulphate from sulphate esters is achieved by hydrolytic enzymes that have been called "sulfatases" or "sulfohydrolases". They are present in soil(Tabatabai and Bremner,1970; Houghton and Rose,1976). Bacteria and fungi appear to be the major sources of these enzymes in the soil(Fitzgerald,1978). If a particular sulfohydrolase is found external to the microbial cell, its action on a sulfate ester will be more likely to yield SO_4^{2-} for plant growth than for microbial growth. Recent studies suggest that several sulfohydrolases are located on microbial cell surfaces(Fitzgerald and Scott,1974; Fitzgerald and George,1977; Murooka et al.,1977; Matcham et al.,1977; Dodgson et al.,1978; Fitzgerald, 1978; Maca and Fitzgerald, 1979).

Arylsulfohydrolases are widely distributed (Dodgson and Rose,1975). Although arylsulfohydrolase activity has been correlated with ester-S in soils (Cooper,1972), evidence from mineralization studies in the past with soils incubated in the absence of plants suggested little or no correlation between its activity and inorganic sulphate released through mineralization(Tabatabai and Bremner, 1972; Freney and Swaby,1975; Kowalenko and Lowe,1975). Though Lee and Speir(1979) later found that arylsulfohydrolase activity was significantly correlated with plant uptake of S from organic sources, they indicated that the evidence was inconclusive. Tabatabai and Al-Khafaji(1979), showed that arylsulfohydrolase activity is inhibited by a variety of trace elements and orthophosphate. Besides its addition as fertilizer, orthophosphate is the end product of P mineralization in soils. Thus the inhibition of this enzyme by orthophosphate may partly explain decreases of arylsulfohydrolase activity observed by Kowalenko and Lowe(1975), the general lack of relationship between arylsulfohydrolase activity and S mineralization, and the slow release of inorganic sulphate during incubation of soils(Tabatabai and Al-Khafaji,1979). Lee and Speir(1979), however felt that since arylsulfohydrolase is presumably only one of the many enzymes involved in the very complex process of organic S mineralization, a direct relationship between its activity and organic S mineralization is perhaps unlikely. Nevertheless, the lack of a consistent

relationship between accumulation of available S and sulfohydrolase activity cannot be interpreted as a lack of role for these enzymes, because they are controlled by end product inhibition and repression by sulphate (McGill and Cole,1981).

Another possible role is that by the hydrolysis of ester sulphates, microbes are protected from the potential toxicity of alkyl sulfates of detergents. Cloves et al.(1980), suggest that the production by a detergent-degrading pseudomonads of an alkylsulfohydrolase which was not affected by either sulphate or cysteine is indicative of this role.

Factors Affecting S mineralization

It has been shown that temperature, moisture, pH(Chaudhry and Cornfield,1967a and b; Williams,1967; Tabatabai and Al-Khafaji,1980), and availability of substrate(Barrow,1960), all affect net S mineralization(Blair,1971; Biederbeck,1978).

Mineralization rate of sulfur was found to increase with temperature from 20 to 35 and 40°C(Williams, 1967; Tabatabai and Al-Khafaji,1980) and to decrease at temperatures less than 10°C and above 40°C(Williams,1967). The effect of pH on mineralization of S is not as consistent as the effect of temperature. Williams(1967) reported that below pH 7.5, the amount of additional S mineralized was proportional to the pH attained following addition of $CaCO_3$,

whereas Tabatabai and Al-Khafaji(1980) found that it was negatively correlated with soil pH in unamended soils.

Sulphur mineralization was considerably retarded at moisture contents appreciably below or above field capacity(Williams,1967), and the optimum for mineralization seemed to be at 60% of the maximum water holding capacity (Chaudhry and Cornfield,1967a).

Cycles of wetting and drying are known to accelerate the decomposition of soil organic matter(Birch,1960); and Barrow(1961), suggests that this is a major factor involved in the increased availability of sulfur under field conditions. A cumulative effect of wetting and drying on S mineralization was found by Williams(1967) in laboratory studies, but cycles of wetting and drying of planted soils in the greenhouse did not stimulate mineralization of sulphur(Freney et al.,1975).

The amount of sulphur mineralized in untreated soils does not appear to be related to carbon, nitrogen or sulphur contents, to C:S, N:S or C:N ratios, or to mineralizable N(Williams,1967; Simon-Sylvestre,1969; Haque and Walmsley, 1972; Jones et al.,1972; Tabatabai and Bremner, 1972). The pattern of release of sulphur from soil organic matter does not appear to be related to any particular soil property, but is probably due to the nature of the decomposing fractions of soil organic matter (Freney and Williams,1980). Nevertheless, results of most incubation studies seem to suggest that larger amounts of S are generally mineralized

from soils with low C/N/S ratios (Harward et al.,1962; Nelson,1964; Haque and Walmsley,1972; Bettany et al.,1974; Kowalenko and Lowe,1975).

Effect of cultivation.

In addition to the factors cited above, cultivation, presence of plants and fertilizer additions have also been reported to affect mineralization of sulphur.

Breaking and cultivation of virgin soil has led invariably to large losses of organic matter(Allison,1973; Campbell et al.,1976). Any change in the organic matter content is likely to be reflected in a change in S status because greater than 90% of the S in noncalcareous soils is present in organic form(Biederbeck,1978). Narrowing of C/N/S ratios upon cultivation has been observed for various soils with some reported changes in S availability(Biederbeck, 1978). This could result in accelerated transformation of the more resistant C-bonded S into the HI-reducible fraction(Biederbeck,1978). The proportions of total S present as HI-reducible S has been found to increase with cultivation(McLaren and Swift,1977; Bettany et al.,1980). These observations would appear to be supported by the work of Freney et al.(1971), who found in an incubation experiment that C-bonded S could be converted to the HI-reducible form. Evidence for this conversion is however indirect and therefore inconclusive.

Effect of Plants and Fertlizer Additions.

Mineralization of S from soil organic matter is influenced by the presence of growing plants. Increases in amounts of S mineralized in the presence of plants than in their absence has been reported in Australia by Freney and Spencer(1960) and Freney et al.(1975), and in New Zealand by Tsuji and Goh(1979). Nicolson(1970), observed not only increased net S mineralization but also a decrease in S loss in the presence of plants.

In the absence of plants immobilization rate of S increased following addition of fertilizer(Freney and Spencer,1960; Saggar et al.,1981). In the presence of plants, however, net mineralization occurred at low levels while net immobilization was observed at very high level of fertilizer addition (Freney and Spencer,1960). At a low level of sulphate fertilizer addition Bettany et al. (1974) noted that mineralization of native soil sulphur was not suppressed under alfalfa cropping.

The stimulating effect of growing plants is obviously of great significance to the cycling of S in the soil-plant system. These increases may be due to greater microbial activity in the rhizosphere of plants and/or to the excretion of enzymes which catalyse the decomposition of soil organic matter(Freney,1967). Removal of end products by plants could stimulate activity of sulfohydrolases, enhancing further release of inorganic S. (McGill and Cole, 1981).

C. COMPARISON OF N AND S MINERALIZATION

In many ways the cycling of S in the soil-plant system resembles that of N. Both cycles have an important atmospheric component and have most of their soil component associated with organic matter, while the very small but active inorganic fraction is subject to a variety of oxidation and reduction reactions. The S cycle differs, however from the N cycle in that the basic natural source of plant available S under natural conditions is the weathering of sulfides of the parent material(Biederbeck, 1978). The nature of the parent material has very little influence on the organic S in surface soils(Scott and Anderson, 1976) but it can markedly affect the amounts and forms of inorganic S(Williams and Steinbergs, 1962; Neptune et al., 1975).

Analogous to the role of nitrate in the N cycle, sulphate holds a key position in the natural cycling of S because under aerobic conditions sulfate is the usual inorganic end product of S metabolism in soils (Anderson,1975).

In view of the close resemblance between microbial conversion of N and S it has been assumed that their proportional rates of mineralization from soil organic matter would be similar (Alexander,1961) and therefore, that N and S would be mineralized in approximately the same ratio as they occur in soil organic matter(Walker,1957; White,1959). This assumption however, fails to explain results of several studies in which the ratio of N/S

mineralized was much greater than that of the soil organic matter(Williams,1967; Tabatabai and Bremner,1972; Haque and Walmsley,1972). There have been reports where the ratio of mineralized N/S was considerably smaller than that of the soil organic matter (Nelson,1964; Simon-Sylvestre,1965), and others in which N was mineralized without any release of S during incubation (Hesse,1957; Barrow,1961). The difference between N and S mineralization in soils is emphazised by the fact that, although the amounts of N and S are highly correlated in soils, most published reports have concluded that the amounts of S mineralized during incubation were not significantly correlated with total N or mineralizable N(Harward et al.,1962; Williams,1967; Haque and Walmsley,1972; Tabatabai and Bremner,1972). Under field conditions Simon-Sylvestre(1965) found a very different mineralization pattern for S than for N with sulphate levels in an uncropped soil undergoing much greater seasonal variations than levels of mineral N. This is in contrast to a recent report of Haynes and Goh(1980), that the seasonal pattern in levels of NO_3^--N and SO_4^{-2}-S showed similar trends in both the surface soil and down the profile. In some incubation studies, a close relationship has been observed between N and S mineralization(Nelson,1964; Kowalenko and Lowe,1975).

Most of the above observations were made with continuous incubation in pots. The only results from the leaching and incubation technique reported by Tabatabai and

Al-Khafaji(1980) support the existence of a close relationship between N and S mineralization as observed by some earlier workers. The N/S ratios of the soils they incubated were however, not significantly correlated with the N/S mineralised. These results in their view, support the suggestion made by Kowalenko and Lowe(1975) and Smith(1976) that although N and S have similarities, they are not parallel metabolic processes. Smith(1976), also reached a similar conclusion.

With the exception of results from Tabatabai and Al-Khafaji's (1980) laboratory experiment and the field results of Simon-Sylvestre(1965) showing faster depletion of organic S than organic N, most results have shown the converse to be true. Another difference in the behaviour of N and S is in their relationship with major soil properties such as C and N contents. While the rate and extent of release of N has been found to be closely governed by these properties, those of S behaved differently (Biederbeck,1978).

It is also possible that N and S mineralization processes may differ due to type and efficiency of microorganisms involved as well as the stability of extracellular enzymes. Williams(1967) observed considerable differences between the degree of suppression of S and N mineralization in response to soil treatment with toluene and formaldehyde. Initial enhancement of S mineralization relatively greater than that of N was also observed after

re-wetting dried soils in the same study. Recently Saggar et al.(1981) reported a net immobilization of S with and without the addition of cellulose or sulfate. In contrast, a concurrent net mineralization of N was observed.

In an attempt to explain the different behaviours of organic N and S during mineralization, Freney et al.(1962) suggested

1. that the N and S mineralized could originate from different fractions of soil organic matter which decompose at different rates.
2. that the ratio of N/S mineralized depends on the N/S ratio of recently added organic matter more than on the ratio in the bulk of the soil organic matter.

McGill and Cole(1981), however, have proposed that mechanisms stabilizing C, N, S and P are not neccessarily common to all four elements. From such a model it was deduced that any element stabilized by mechanisms different from those of other elements may accumulate at a rate independent of other elements. Sulphur is found in organic matter in two main forms, as ester linkages and as direct S to C bonds, whereas N is directly bonded to C. A dual mechanism for S mineralization but not for N mineralization will therefore go a long way to explain the lack of consistent relationship and stoichiometry between N and S mineralization. Thus they proposed that C and N are stabilized together and mineralized through biological mineralization, whereas organic P and sulphate esters are

stabilized independently of the organic moiety and are mineralized through biochemical mineralization. C-bonded S appears to be controlled by mechanisms similar to those for N.

The salient features of the above proposal are that mineralization of N and C-bonded S occur only when soil organisms are required to use N or S rich materials as an energy source, while the release of sulphate from sulphate esters by sulfohydrolases, is controlled by the need for S and not strictly by the need for C as occurs with N. Additionally, changes in ratios of N:S should be inversely proportional to ratios of HI-reducible S:C-bonded S because of closer link between N and C-bonded S than HI-reducible S.

III. MATERIALS AND METHODS

A. SOILS

The soils used in this study were surface soils(0 to 15cm) selected from Chernozemic and Luvisolic soil orders and were sampled in the fall of 1981.

Samples were taken from cultivated and virgin soils of three Great Groups within the Chernozemic order, and two plots each from the east side of series E and series F of the Breton plots to represent the Luvisolic order. Descriptions of these soils and relevant analytical data are shown in Table 1.

Samples of these field-moist soils were passed through a 2 mm screen, and divided into two portions. One portion was placed in a polythene bag and stored in a cold room at 5°C for use later to conduct incubation experiments. The second portion was air dried at room temperature and then stored in plastic containers. A sub-sample of this air-dried portion was later ground to pass a 100 mesh sieve for analysis.

B. INCUBATION EXPERIMENTS

Two methods of incubation were conducted to study the mineralization of N and S. These were the methods of continuous incubation and incubation and leaching, i.e. intermittent incubation.

Table 1: Properties of Soils Used

Soil Location and Great Group	Soil Series and Soil Sample No.	pH	Total C %	Total N %	Total S %	Total P %	Clay %	Silt %	Sand %	Textural Classification	Ca+Mg+K meq/100g
Black Chernozem											
Ellerslie V	Malmo (1)	6.5	10.77	0.7928	0.1187	0.1029	39	41	20	Silty Clay Loam	67.1
Ellerslie C	Malmo (2)	6.6	6.95	0.5268	0.0733	0.0969	38	42	20	Silty Clay Loam	54.1
Ponoka V	Peace Hills (3)	6.7	4.72	0.2618	0.0397	0.0539	6	14	80	Loamy Sand	26.8
Ponoka C	Peace Hills (4)	6.8	5.00	0.3387	0.0473	0.0629	6	14	80	Loamy Sand	27.9
Dark Brown Chernozem											
Lethbridge V	Lethbridge (5)	7.5	2.97	0.2504	0.0566	0.0874	35	25	40	Clay Loam	30.9
Lethbridge C	Lethbridge (6)	7.2	2.27	0.1667	0.0484	0.0656	34	36	30	Clay Loam	34.6
Standard V	(7)	7.0	3.09	0.2652	0.0504	0.0721	63	27	10	Heavy Clay	62.8
Standard C	(8)	7.2	2.88	0.2481	0.0721	0.0709	61	28	11	Heavy Clay	61.5
Brown Chernozem											
Chin V	(9)	7.2	2.25	0.1781	0.0381	0.0540	20	16	64	Sandy Loam	24.1
Chin C	(10)	7.1	2.39	0.1707	0.0392	0.0534	16	22	62	Sandy Loam	21.2

Table 1: (con't)

Soil Location and Great Group	Soil Series and Soil Sample No.	pH	Total C	Total N	Total S	Total P	Clay	Silt	Sand	Textural Classification	Ca+Mg+K meg/100g
			%				%				
Vauxhall V	(11)	6.9	2.41	0.1849	0.0361	0.0424	12	30	58	Sandy Loam	21.5
Vauxhall C	(12)	7.2	1.54	0.1306	0.0400	0.0413	14	38	48	Loam	22.6
Gray Luvisol											
Breton (Series 'E' 3)	Breton (13)	7.0	1.33	0.1108	0.0173	0.0684	20	42	38	Loam	22.3
Breton (Series 'E' 5)	Breton (14)	6.9	1.12	0.0975	0.0151	0.0517	18	37	45	Loam	21.0
Breton (Series 'F' 3)	Breton (15)	6.8	2.11	0.1721	0.0252	0.0606	16	45	39	Loam	22.1
Breton (Series 'F' 5)	Breton (16)	6.8	1.99	0.1539	0.0211	0.0567	16	45	39	Loam	23.2

Breton Series 'E' 3 - Wheat Fallow Rotation, Fertilized Plot.

Breton Series 'E' 5 - Wheat Fallow Rotation, Unfertilized Plot.

Breton Series 'F' 3 - Continuous Cropping, Fertilized Plot.

Breton Series 'F' 5 - Continuous Cropping, Unfertilized Plot.

Fertilizer Application Rates (Breton plots) (History)

(a) 1944-1963 - Fertilizer was applied every second year at rates of approximately N-9, P-5, K-14and S-8 kg/ha each year.

(b) 1963-1981 - Fertilizer was applied each year at N-11, P-6, K-16 and S-9 kg/ha.

Continuous Cropping - Wheat, Oats, Barley, Hay, Hay Rotation.

V = Virgin C = Cultivated

Continuous Incubation

Samples of 100 g (oven-dry basis) of moist soils were weighed into plastic containers(11.0 cm in diameter and 7.5 cm high). Deionised water was added to bring each soil sample to its respective field capacity moisture content and mixed thoroughly. A plastic lid with a small hole(6 mm in diameter) in the centre for aeration was used to cover the containers. Containers were weighed once every week and deionised water added to restore initial weight.

The number of containers used corresponded to the number of sampling times with three replicates for each soil. This permitted the disposal of containers from which samples were taken at each sampling time. Samples of 20 g were taken from three pots for each soil at intervals of two weeks for twenty weeks and transferred into 125 ml plastic bottles. The samples were extracted by shaking for 1 hour in 50 ml of 0.1M KCl. The suspension was then filtered through a Whatman no. 42 filter paper and aliquots taken for determination of NH_4^+-N and NO_3^--N and SO_4^{-2}-S. Temperature varied between 22 and 25°C in the incubation room during the incubation period.

Incubation and Leaching

Triplicate moist samples(20 g oven-dry basis) brought to their respective field capacities with deionized water were mixed thoroughly with an equal weight of washed Ottawa sand. Soil and sand mixtures were then transferred into

Buchner funnels (5.7 cm in diameter and 3.0 cm in height) lined with fibre glass filter.

Buchner funnels were placed on 125 ml suction flasks using no. 3 filter adapters. A filter paper was placed over the mixture of soil and sand to avoid dispersing the mixture when extracting solution was added. A pre-incubation leaching with 0.01M KCl was then used to remove mineral-N and S by the following procedure:

1. 15 to 20 ml of 0.01M KCl was poured onto the mixture.
2. solution was allowed to soak into the mixture.
3. suction was then turned on and as much solution as possible was removed.

The above steps were repeated three times. Leachates' volumes ranged from 46 to 48 ml. Suction was used to remove excess moisture to restore samples to field capacity and funnels were covered with Parafilm which had a small hole in the centre for aeration. Funnels were then incubated at a temperature range of 22 to 25°C for a period of 22 weeks. The leaching and incubation procedure was repeated following 2,4,6,8,10,14,18 and 22 weeks. Funnels were weighed once every week and deionised water added to restore initial weight.

Aliquots from the initial and subsequent leachings were taken for determination of total mineral-N(NH_4^+-N, NO_2^--N and NO_3^--N), SO_4^{-2}-S and organic N.

C. ANALYTICAL PROCEDURES

Total mineral N(NH_4^+-N, NO_3^--N and NO_2^--N) was determined on soil extracts and leachates using the steam distillation method of Bremner(1965b), and SO_4^{-2}-S was determined by the method of Johnson and Nishita(1952) as modified by Dean(1966).

Total C was determined on soil samples using the LECO (Laboratory Equipment Corporation) total C analyser (CR-12,Model 781- 800).

Total N was estimated by Kjeldahl digestion of soil samples on a block digestion apparatus to convert N to ammonium and the ammonium was analysed with a Technicon Auto-Analyser II system(Schuman et al.,1973).

Organic N plus NH_4^+-N in the leachates were estimated by the method of Schuman et al.(1973) for total N in soil samples with modification. Ten ml of leachate was taken and preheated to 200°C for removal of excess water before digestion and subsequent determination of NH_4^+-N. Organic N leached was then estimated as the difference between NH_4^+-N determined on digested leachates with the Technicon Auto-Analyser and NH_4^+-N determined on aliquots of undigested leachates by steam distillation. Nitrates in the leachates would not be reduced to ammonium since there was no pretreatment with Fe or any other suitable reducing agent(Bremner,1965; Kowalenko,1975). Preliminary investigation using known amounts of amino acids and nitrates showed that while recovery of amino acids ranged from

94-102%, recovery of the added nitrates without pretreatment with Fe was negligible or nil.

Total S and total P were determined by fusion with alkali metal nitrates (a mixture of $NaNO_3$ and KNO_3), and later extracted with acid to bring sulfate into solution and hydrolyse phosphate to orthophosphate(McQuaker and Fung,1975). The extracts were then analysed for sulphur and phosphorus using an Inductively Coupled Plasma with a vacuum spectrometer.

HI-reducible S was measured as described by Freney(1969) with measurement of the H_2S evolved by the method of Dean(1966) and C-bonded S was estimated as the difference between total S and HI-reducible S.

Amount of exchangeable cations in the various soil samples were determined by using 1N NaCl as the extractant(McKeague,1978). Initial attempts to determine the concentrations of Ca, Mg and K in the extracts by Atomic Absorption spectrometry were futile. This might be due to the high salt concetration of the extractant (1N NaCl) which may have caused spectral interferences. Hence, extracts were analysed using an Inductively Coupled Plasma-Atomic Emission Spectrometer. This instrument has been shown to have minimal spectral interferences and an extensive linear dynamic range(Dahlquist and Knoll, 1978).

Soil pH was measured with a pH meter using a glass electrode in a 1:2 soil to 0.01M $CaCl_2$ suspension(McKeague, 1978).

The moisture content at 33kpa soil moisture tension was determined by the porous plate method(McKeague, 1978).

IV. RESULTS AND DISCUSSION

Results from incubation studies showed different mineralization dynamics for organic N and S in all soils. Mineralization kinetics will be discussed separately for each element, and then a comparison will be made of these observations for the two elements. Cultivation, fallowing, and fertilizer applications were observed to have had significant effects on organic matter fraction distributions. The significance of these trends in relation to organic matter transformations will be assessed.

A. NITROGEN

Trend of Mineralization

Different trends of mineralization were observed for N using the two methods of incubation(Figs. 1.01 to 1.16). The N mineralization time curves obtained with continuous incuabtion were inconsistent. Net amounts of N mineralized(i.e. N mineralized during time 't'- initial N in soil at time 't'=0) were not constant after each interval of sampling. Subsequent amounts of net N mineralized either decreased or increased in relation to previous amounts. The rate of N mineralization in soils is not constant(Harmsen and Van Schreven,1955). In the incubation and leaching technique also amounts of mineral N leached were not constant after each interval of incubation. Unlike amounts

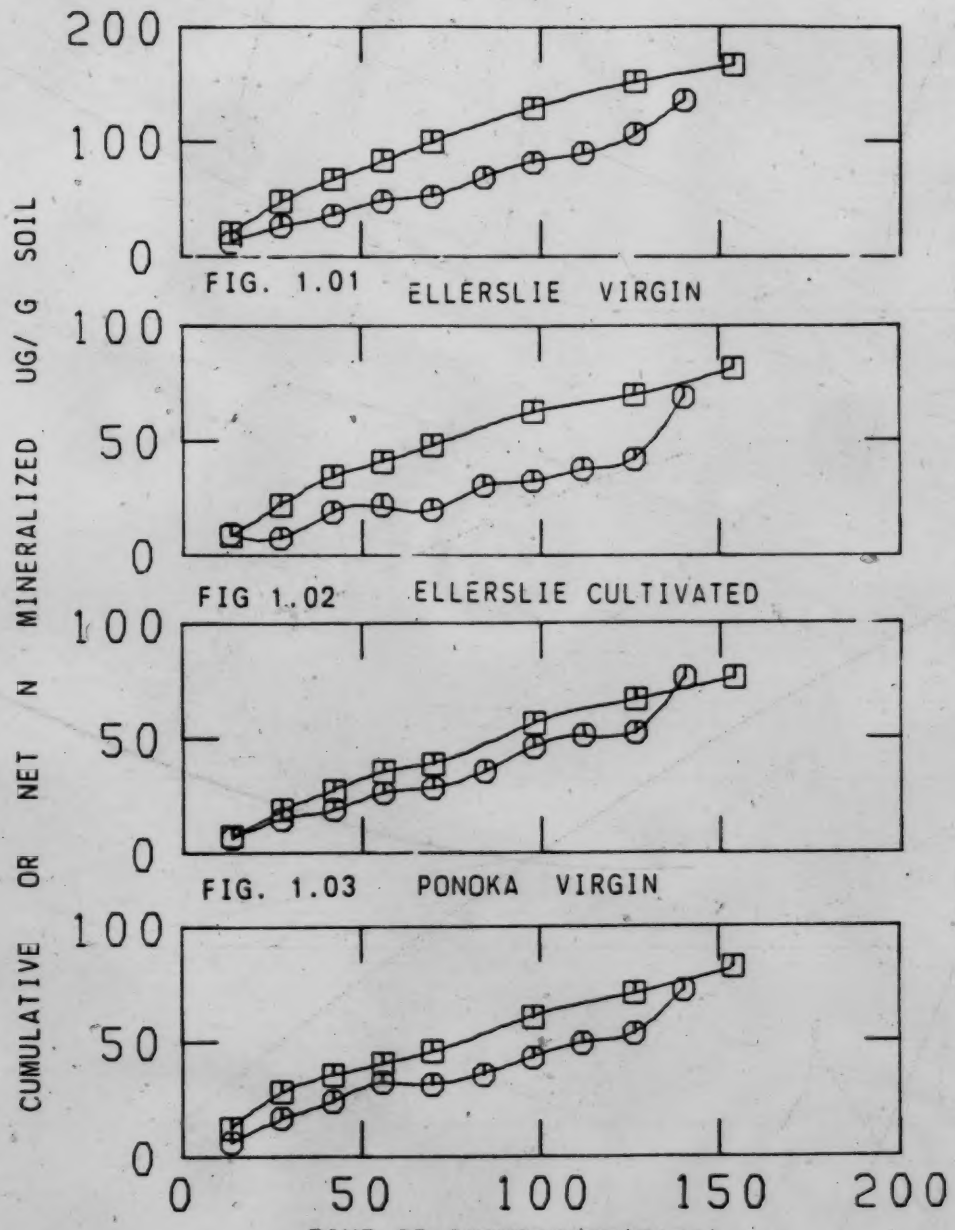

FIG. 1.04 PONOKA CULTIVATED

Figs. 1.01, 1.02, 1.03 and 1.04 represent cumulative or net amounts of N mineralized in above soils with time of incubation.

CONTINUOUS INCUBATION(NET N) — —⊖—⊖—

INCUBATION AND LEACHING(CUMULATIVE N) — —⊡—⊡—

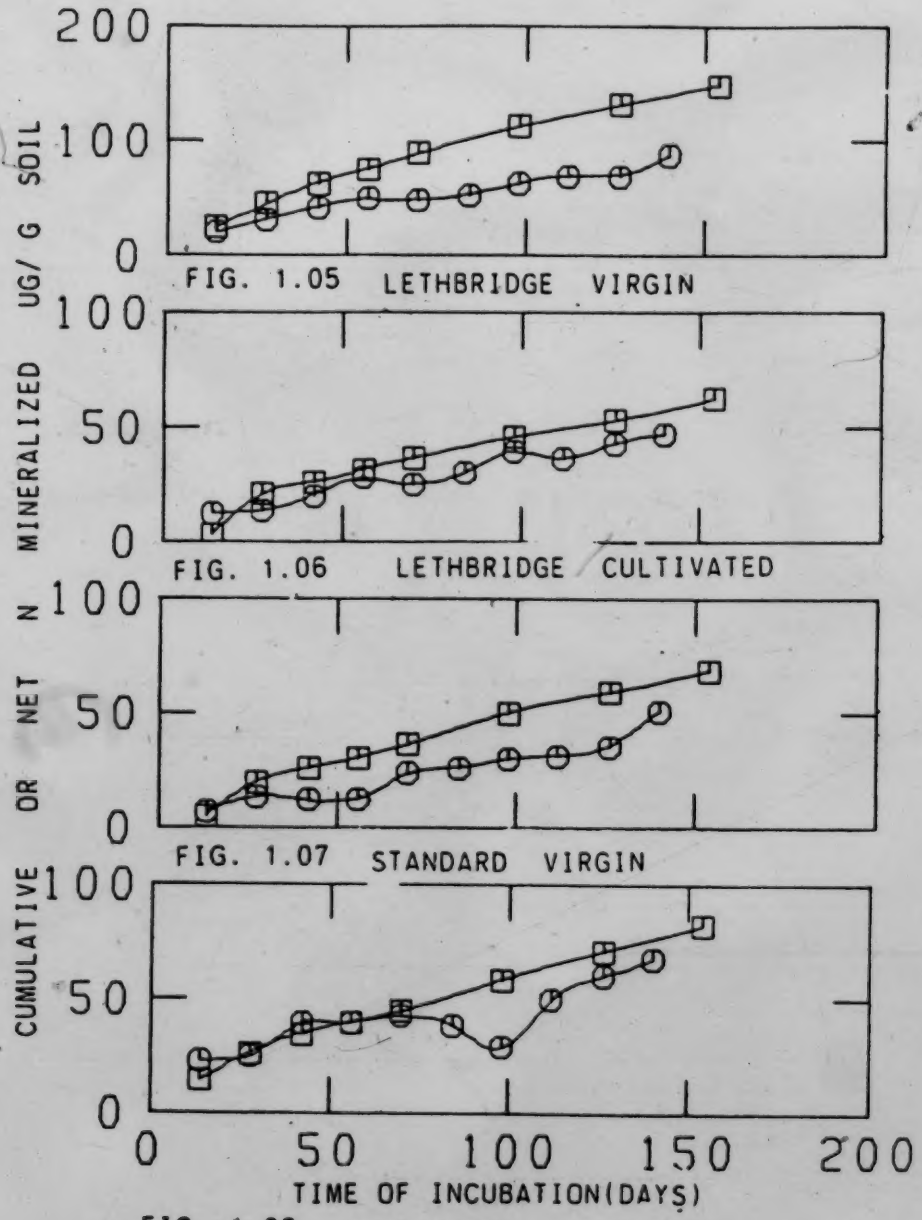

FIG. 1.08 STANDARD CULTIVATED

Figs. 1.05. 1.06, 1.07 and 1.08 represent cumulative or net amounts of N mineralized in above soils with time of incubation.

INCUBATION AND LEACHING(CUMULATIVE N)

CONTINUOUS INCUBATION(NET N)

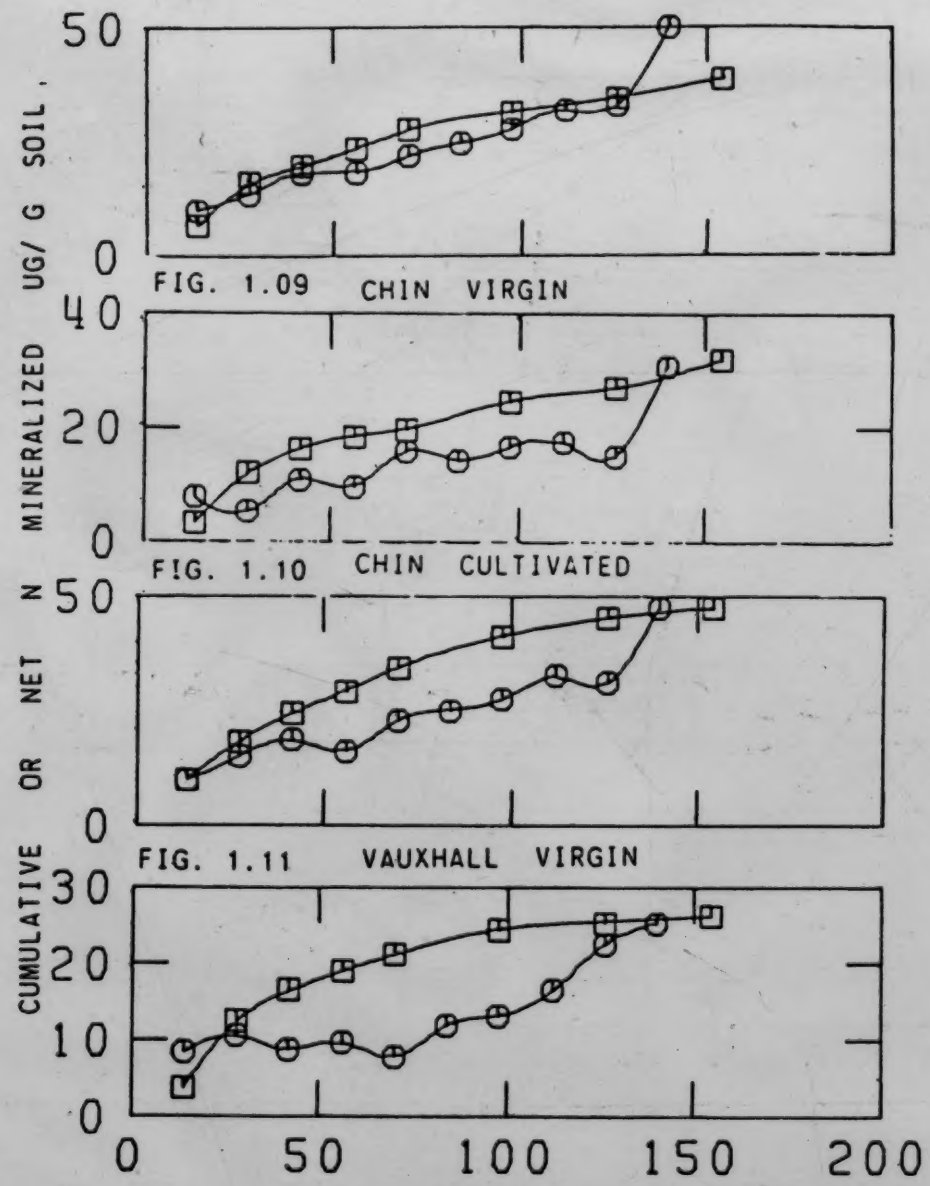

FIG. 1.09 CHIN VIRGIN

FIG. 1.10 CHIN CULTIVATED

FIG. 1.11 VAUXHALL VIRGIN

FIG. 1.12 VAUXHALL CULTIVATED

Figs. 1.09, 1.10, 1.11 and 1.12 represent cumulative or net amounts of N mineralized in above soils with time of incubation.

INCUBATION AND LEACHING(CUMULATIVE N) — -⊕——⊕-

CONTINUOUS INCUBATION(NET N) — -⊙——⊙-

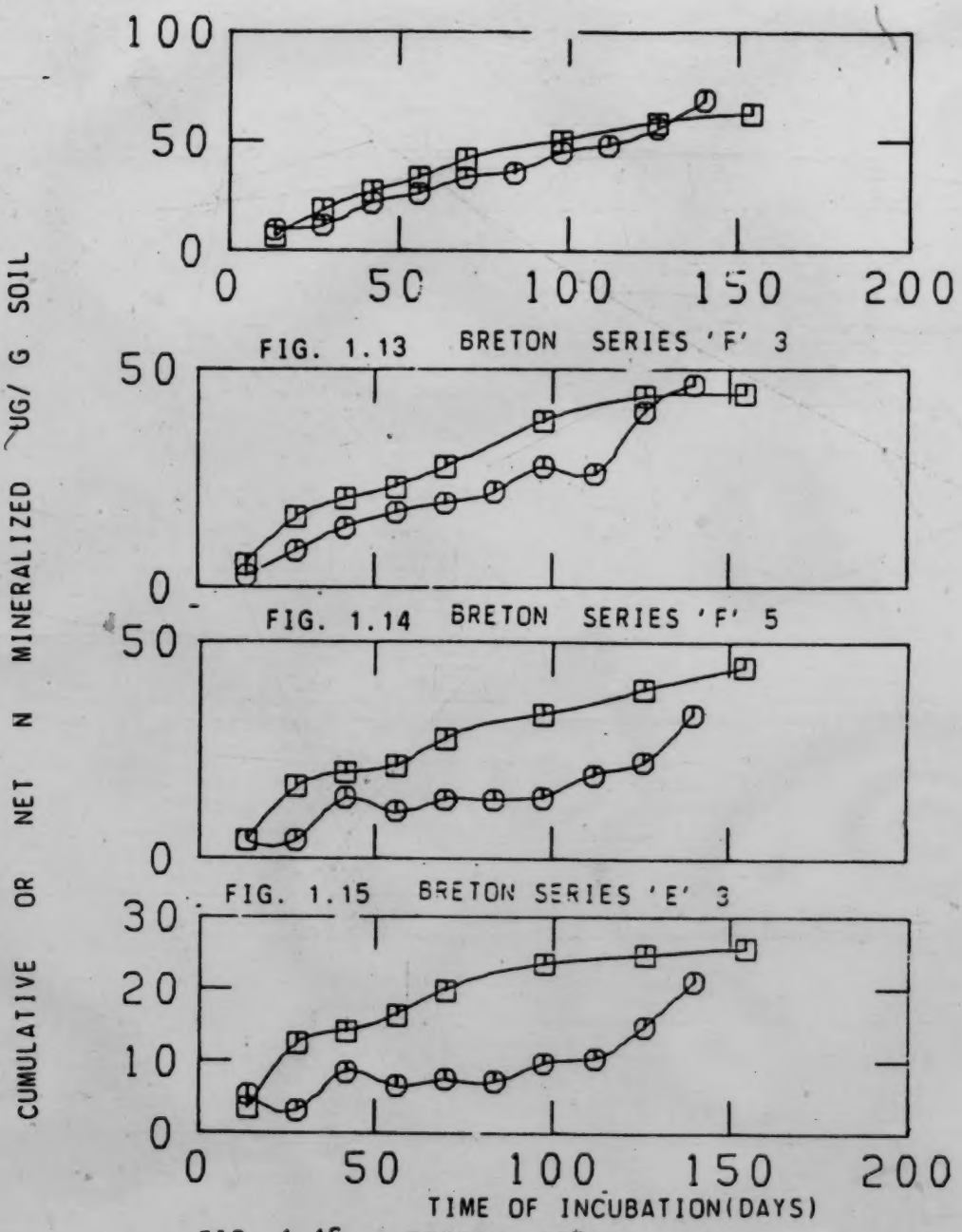

FIG. 1.13 BRETON SERIES 'F' 3

FIG. 1.14 BRETON SERIES 'F' 5

FIG. 1.15 BRETON SERIES 'E' 3

FIG. 1.16 BRETON SERIES 'E' 5

Figs. 1.13, 1.14, 1.15 and 1.16 represent cumulative or net amounts of N mineralized in above soils with time of incubation.

INCUBATION AND LEACHING(CUMULATIVE N) —

CONTINUOUS INCUBATION(NET N) ····

of net N mineralized with the continuous incubation, however, these amounts found in leachates generally decreased with each interval of incubation. These decreases would however appear to be enhanced to varying degrees in each soil sample by the leaching of labile organic N concurrently with inorganic N mineralized. Smith et al.(1980) suggested that leaching of labile organic N would lower subsequent values for N mineralization. Totalling the amounts of mineralized N found in successive leachings (referred to as cumulative amounts of N mineralized) after each interval of incubation, curvilinear relationships between cumulative N mineralized and time were found(Figs 1.10 to 1.25). Plots of cumulative amounts of N mineralized against the square root of time were however found to be linear in most of the soils(Figs 2.01 to 2.04). Similar observations have been reported by Stanford and Smith (1972), Cassman and Munns(1980) and Campbell et al.(1981). There is no fundamental significance ascribed to the observed linear relationships, although it may be noted that diffusion-controlled reactions display similar characteristics(Stanford and Smith, 1972). In contrast, Tabatabai and Al-Khafaji(1980) observed a linear relationship between cumulative N mineralized and time.

Observations from this study with the continuous incubation method are consistent with earlier criticisms levelled against its use in N mineralization studies. The N mineralization time curves and data obtained cannot provide

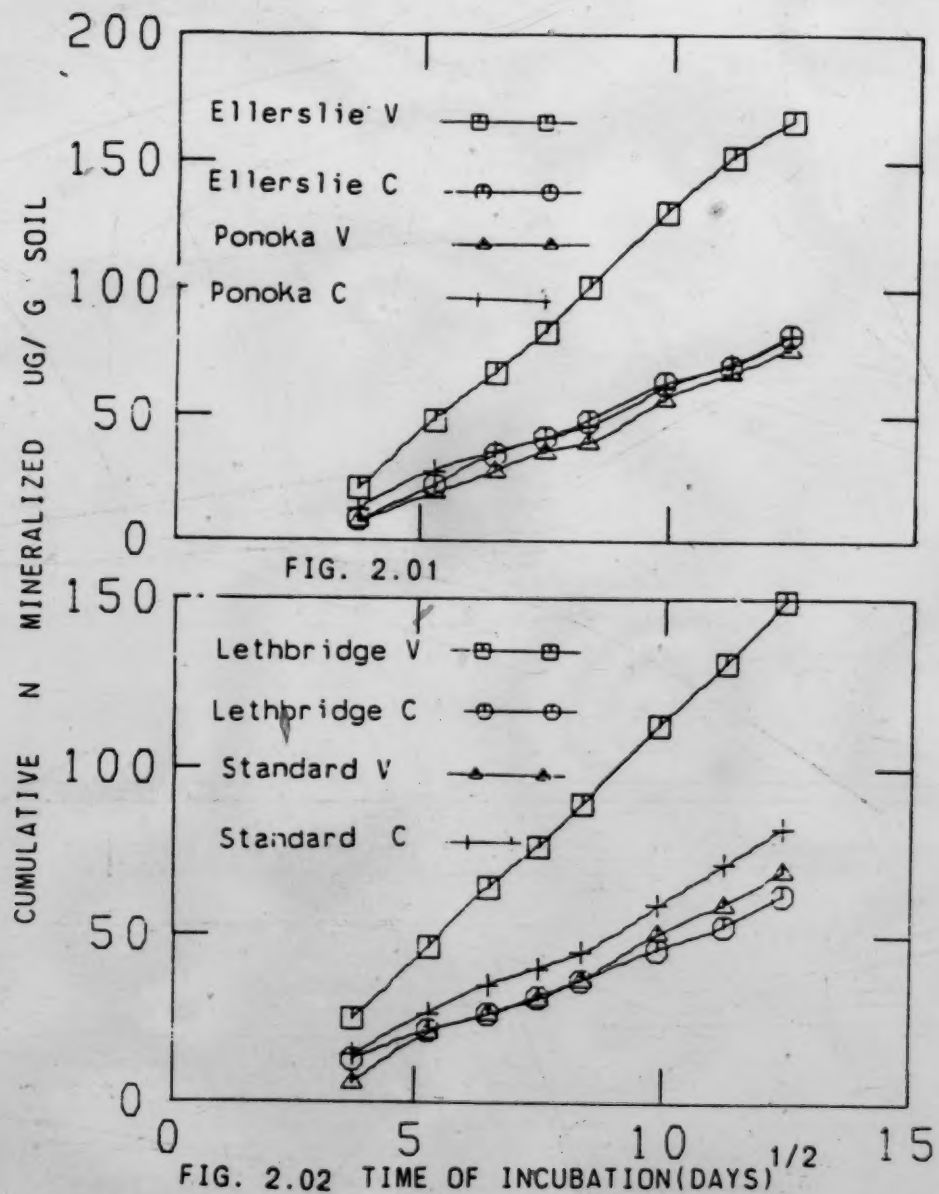

FIG. 2.01

FIG. 2.02

Figs. 2.01 and 2.02 show the linear relationships between cumulative amounts of N mineralized and the square root of days of incubation in soil samples from the Black and Dark Brown zones respectively.

C-- CULTIVATED SOILS
V-- VIRGIN SOILS

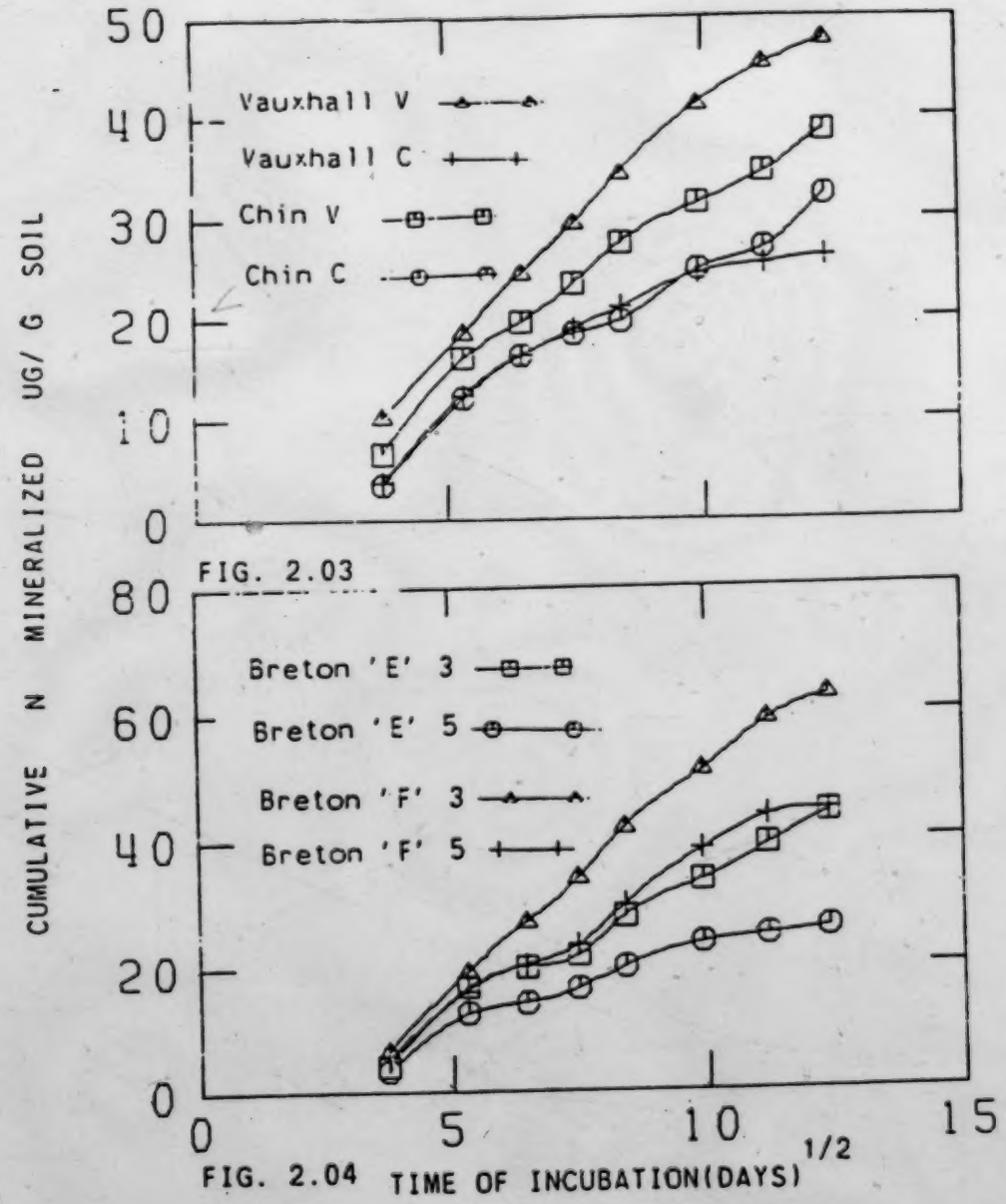

FIG. 2.03

FIG. 2.04

Figs. 2.03 and 2.04 show the linear relationships between cumulative amounts of N mineralized and the square root of days of incubation in soil samples from the Brown zone and the Breton plots

C-- CULTIVATED SOILS
V-- VIRGIN SOILS

a rational or consistent basis for estimating long-term N-supplying capacities of soils(Stanford and Smith,1972) and they do not conform to the characteristics of first order kinetics. During earlier studies of N mineralization capabilities of soils using this approach, cumulative inhibitory effects on N mineralization sometimes arose during incubation. For example, Allison and Sterling(1949) observed appreciable drops in pH during 23 week continuous incubation. In some cases, accumulation of toxins has been suspected (Acharya and Jain,1955). Similar inhibitory effects would seem to have occurred resulting in decreases in amounts of N mineralized observed sometimes during the period of incubation in this study. Rate of mineralization is affected by supply of oxygen. Manipulation of soil samples prior to incubation may conceivably alter porosity, especially in soils possessing relatively unstable structure. Moreover the addition of water and stirring to accomplish uniformity in moisture distribution, as practised under conditions of continuous incubation, adds to the uncertainty of aeration control (Stanford and Hanway,1953). Fluctuations in amounts of oxygen supplied might thus also contribute to the inconsistencies in the N mineralization time curves observed with the continuous incubation method.

Removal by suction of excess solution might cause compaction of soils having a high proportion of water-unstable aggregates. In the incubation and leaching technique, compaction has been minimized by mixing sand with

the soil sample. In the original procedure used by Stanford and Hanway(1953), vermiculite was used instead of sand.

In view of the above shortcomings of continuous incubation which led Stanford and Smith(1972) to propose the use of the leaching and incubation for studies of N-mineralization capabilities of soils, further discussion of results will be limited to observations from this method.

Cumulative amounts of N mineralized ranged from 25.6 in a Breton plot (Gray Luvisol) to 166.5 ug N/g soil in a Black Chernozemic soil at the end of the 22 weeks incubation period. Expressed as percentages of total N, these ranged from 1.6 to 5.9%(Table 2). This is in agreement with a range of 1.8 to 6.7% reported by Tabatabai and Al-Khafaji(1980) for 12 soils in Iowa incubated at 20°C for 26 weeks. At higher temperatures of 35°C, Smith et al.(1980) found the range to be between 5 and 11% for a period of 11 weeks and Tabatabai and Al-Khafaji(1980) reported a range of 8.3 to 26.8%.

The cumulative amounts of N mineralized after 22 weeks of incubation in this study were significantly correlated at 1% level of probability with total C(r=0.75) and total N(r=0.77) but not with C/N(r=0.15)(Table 3). Elemental ratios are of little value in predicting rates of mineralization(Swift, 1976). In contrast Tabatabai and Al-Khafaji(1980) reported that cumulative amounts of N mineralized were not correlated with organic C or total N.

Table 2: Nitrogen leached after 22 weeks as a percent of total N present in soils.

Soil Type	Mineral N Leached	Organic N Leached	Total N Leached
	% of total N Present		
Ellerslie Virgin	2.1	0.5	2.6
Ellerslie Cultivated	1.6	0.6	2.1
Ponoka Virgin	2.9	1.7	4.6
Ponoka Cultivated	2.4	0.7	3.1
Lethbridge Virgin	5.9	1.2	7.2
Lethbridge Cultivated	3.7	1.6	5.4
Standard Virgin	2.6	1.3	3.9
Standard Cultivated	3.3	1.3	4.6
Chin Virgin	2.2	1.6	3.8
Chin Cultivated	1.9	1.0	2.9
Vauxhall Virgin	2.6	1.6	4.2
Vauxhall Cultivated	2.0	1.4	3.4
Breton Series 'E' 3	3.9	1.8	5.7
Breton Series 'E' 5	2.6	1.8	4.4
Breton Series 'F' 3	3.6	1.2	4.8
Breton Series 'F' 5	2.9	1.7	4.6

Table 3: Correlation coefficients between pairs of properties in all soils used.

	Total C	Total N	Total S	C-O-S	C-S	C/N	C/S	N/S	NM	SM
NM/SM	0.592**	0.537**	0.355**	0.386**	0.189*	0.561**	0.482**	0.299**	0.464**	-0.391**
SM	0.246**	0.300**	0.541**	0.529**	0.530**	-0.561*	-0.246**	-0.245**	0.525**	
NM	0.750**	0.771**	0.793**	0.799**	0.673**	0.154	0.182	0.115		
N/S	0.355**	0.322**	-0.098	-0.078	-0.166*	0.211**	0.897**			
C/S	0.480**	0.387**	0.002	0.023	-0.084	0.615**				
C/N	0.402**	0.255**	0.139	0.146	-0.092					
C-S	0.739**	0.777**	0.900**	0.848**						
C-O-S	0.871**	0.903**	0.994**							
S	0.866**	0.899**								
N	0.987**									

** Indicates significance at 1% level of probability

* Indicates significance at 5% level of probability

NM - Cumulative N mineralized

SM - Cumulative S mineralized

Cumulative amounts of N mineralized have been used by various workers to estimate the N mineralization potentials(No) of soils(for example, Stanford and Smith ,1972; Oyanedel and Rodriguez,1977; Campbell et al.,1981; Campbell and Souster,1982). The basic concept is that the amount of N mineralized is proportional to No;i.e. $dN/dt=-kN$.

Organic N in Leachates

Solution leached through incubated soil samples contains organic N compounds which may be readily mineralizable(Legg et al.,1971; Broadbent and Nakashima,1971).

Total organic N leached at the end of the 22 week period in this study ranged from 16.9 to 43.2 ug N/g soil. This was 21 to 75% of total cumulative N mineralized, 19 to 43% of total N in leachates(Table 4) and 0.5 to 1.8% of total N present in soils used for this study(Table 2). Smith et al.(1980) from an incubation period of 11 weeks reported for three soils leached with 30 ml of 0.01M $CaCl_2$ and 25 ml of minus N nutrient solution, a range of 13.8 to 42.0% as much leached organic N as leached mineral N.

N Mineralization Potentials, No

It is common practice in science to try to explain natural phenomena by models. More sophisticated models depend on mathematical statements and, consequently allow us

Table 4: Comparison of Amounts of Leached Mineral N and Leached Organic N as Percentages of Total N Leached Following 22 Weeks of Incubation.

Soil Type	Mineral * N Leached	Organic * N Leached	Leached Organic N / Leached Mineral N x 100	Leached Organic N / Leached Total N x 100	Leached Mineral N / Leached Total N x 100
	ug N g^{-1} soil		%		
Ellerslie Virgin	166.5±7.0	39.9±0.4	23.9	19.3	80.7
Ellerslie Cultivated	81.6±3.5	30.6±5.8	37.5	27.3	72.7
Ponoka Virgin	76.6±2.8	43.2±2.0	56.4	36.1	63.9
Ponoka Cultivated	82.0±5.6	25.1±3.2	30.6	23.4	76.6
Lethbridge Virgin	149.4±5.3	31.2±1.3	20.9	27.3	82.7
Lethbridge Cultivated	62.3±3.1	27.1±2.2	43.5	30.1	69.9
Standard Virgin	69.2±1.9	33.3±1.7	48.1	32.5	67.5
Standard Cultivated	82.0±7.9	31.1±3.6	37.9	27.5	72.5
Chin Virgin	38.8±0.7	29.0±1.7	74.7	42.7	57.3
Chin Cultivated	32.2±4.2	16.9±1.6	52.5	34.4	65.6
Vauxhall Virgin	47.6±1.9	29.5±2.3	61.9	29.1	70.9
Vauxhall Cultivated	26.2±2.6	18.1±1.9	69.1	40.6	59.4

Table 4: (con't)

Soil Type	Mineral * N Leached	Organic * N Leached	Leached Organic N / Leached Mineral N x 100	Leached Organic N / Leached Total N x 100	Leached Mineral N / Leached Total N x 100
	ug N g^{-1} soil		%		
Breton Series E Plot 3	44.2±4.2	19.8±1.9	44.8	30.9	79.1
Breton Series E Plot 5	25.8±2.0	17.3±2.4	67.1	40.1	59.9
Breton Series F Plot 3	62.6±3.5	21.2±3.0	33.8	23.9	76.1
Breton Series F Plot 5	44.6±0.9	25.4±2.8	59.1	37.2	62.8

* Entries are means of three replicates ± standard deviations.

not only to explain observable facts but also to predict possibly unobserved events. Figs. 1.01 to 1.16 show that N mineralization time curves obtained with the incubation and leaching technique bend down in a way that suggests a constant percentage loss. This means that the amount of inorganic N released through mineralization is proportional to the amount present at the beginning of the period. These observations are consistent with data in the literature suggesting that N mineralization reactions follow first order kinetics(Jenny, 1941; Stanford and Smith, 1972; Smith et al., 1980; Campbell et al., 1981).

First order kinetics can be described by the equation

$$dN/dt=-kN \quad -----(1)$$

where

N=concentration of mineralizable substrate

k=rate constant for mineralization

t=time

Upon integration from time 't0' to time 't' this yields

$$Nt=Noexp(-kt) \quad -----(2)$$

where

No=beginning substrate concentration

Nt=substrate concentration at time 't'

The beginning substrate concentration No and Nt are both unknown, therefore it is convenient to eliminate one unknown using the relation

$$Nt=(No-Nm) \quad ----(3)$$

where

Nm=N mineralized in time period 't'

Using the substitution in Eq. 2 we obtain

$$No-Nm=Noexp(-kt)--------(4)$$

In statistics, a common model describing the makeup of an observation states that it consists of a mean plus an error. This is the linear additive model. A minimum assumption is that the errors are random, that is, the population of Ys is sampled at random(Steel and Torie,1977). The simplest linear additive model is given by

$$Yi=u+\epsilon i---------(5)$$

This states that the ith observation,Yi, consists of a mean u plus an error ϵi. The errors are assumed to be from a population of ϵs with mean zero. That the sampling errors be uncorrelated is a theoretical requirement for valid inferences to be made about a population and is assured by drawing the sample in a random manner(Steel and Torrie,1977).

The exponential model Eq(4) describing N mineralization has been commonly transformed (Stanford and Smith.,1972; Oyanedel and Rodriguez, 1977; Herlihy, 1979) to the form

$$log(No-Nm)=logNo-k/2.303(t)----(6)$$

This was done to linearize the model, make the error term additive and make it normally distributed in conformity with the properties of errors stated earlier. Stanford and Smith(1972) by this transformation assumed that the errors in their mineralization studies were multiplicative.i.e. large errors were associated with large values of

mineralized N. Their model according to Talpaz et al(1981) is

$$No-Nm=Noexp(-kt).\epsilon \text{--------(7)}$$

where

ϵ=the error term.

In N mineralization studies this assumption is invalid because errors are not correlated with time of sampling or mean values of N mineralized(Smith et al.,1980; Talpaz et al.,1981). This is similar to observations made earlier about errors in a linear model. The appropriate model is therefore

$$No-Nm=Noexp(-kt)+\epsilon \text{----------(8)}$$

This model gives more reliable estimates of No and k and smaller deviations of data from a best fit curve(Talpaz et al.,1981; Smith et al.,1980). The use of Stanford and Smith's technique leads to an overestimation of No and subsequently an underestimation of k. Thus using this approach, i.e. Eq(8) to analyze Stanford and Smith's data, Talpaz et al.(1981) found lower and higher values for No and k respectively than those reported by Stanford and Smith(1972) with equation (7).

Equation (8) cannot be linearized with respect to k, hence regression by ordinary least squares method cannot be applied. No and k have therefore been estimated by non-linear regression (Smith et al.,1980; Talpaz et al.,1981). This requires the use of computerized curve fitting techniques. In this study, No and k estimates were

obtained using the BMDP computer program PAR. BMDP programs usually analyse data by an iterative 'examine and modify' series of steps. PAR is a nonlinear regression program which estimates the parameters of a nonlinear function by least squares and can be used to compute maximum likelihood estimates. It is appropriate for a wide variety of problems that are not well represented by equations with linear parameters(Ralston, 1977; 1981). '

As shown in Table 5, values for No and k were estimated with both cumulative N mineralized alone, and cumulative N mineralized plus organic N leached at various times of leaching as stated in the Materials and Methods section. Values of No calculated with cumulative mineralized N alone ranged from 53.7 to 85.2% of No estimated with total N leached (Table 5). Because the leached organic N is considered mineralizable, the most appropriate estimates of No and k are given by cumulative N mineralized plus organic N leached.

Estimates of No therefore ranged from 50.5 to 286 ug N/g soil(Table 5). Talpaz et al.(1981) using the non-linear regression approach to analyze Stanford and Smith's (1972) data for 39 soils found a range of 15 to 253 ug N/g soil, while Campbell et al.(1981) reported a range of 67-256 ug N/g soil in Queensland. In a recent study, Campbell and Souster(1982) estimated a range of 66 to 401 ug N/g soil for some Saskatchewan soils using only cumulative N mineralized.

'Copy of the program can be obtained from Ray Weingardt (Programmer), Animal Science Dept, University of Alberta.

Table 5: Comparison of estimates of mineralization potential, No(ug N/g soil), mineralization rate constants, k, and their standard deviations (S) from values of cumulative mineralized N (A) and total N leached (B).

	(A)			(B)			
	No* ug N/g soil	K* week^{-1}	S* ug N/g soil	No ug N/g soil	K week^{-1}	S ug N/g soil	$\frac{No^*}{No} \times 100$
Ellerslie Virgin	243.4	0.0535	2.08	285.7	0.0584	1.584	85.2
Ellerslie Cultivated	114.3	0.0554	1.98	147.1	0.0614	1.680	77.7
Ponoka Virgin	146.5	0.0338	1.54	201.6	0.0414	2.350	72.7
Ponoka Cultivated	107.2	0.0619	2.87	143.6	0.0627	3.690	74.7
Lethbridge Virgin	194.8	0.0634	2.58	240.4	0.0609	4.460	81.0
Lethbridge Cultivated	76.2	0.0699	2.33	99.4	0.0886	4.180	76.7
Standard Virgin	119.3	0.0390	2.11	150.7	0.0511	2.740	79.2
Standard Cultivated	113.9	0.0549	3.26	143.0	0.0655	4.590	79.6
Chin Virgin	41.7	0.1061	1.09	77.7	0.0934	2.750	53.7
Chin Cultivated	35.8	0.0888	1.62	53.9	0.0965	1.530	66.4
Vauxhall Virgin	55.1	0.0976	0.62	89.4	0.0869	1.860	61.6
Vauxhall Cultivated	28.8	0.1439	1.60	51.3	0.0939	1.720	56.1

Table 5: (con't)

	(A)			(B)			
	No* ug N/g soil	K* week^{-1}	S* ug N/g soil	No ug N/g soil	K week^{-1}	S ug N/g soil	$\frac{No^*}{No} \times 100$
Breton Series 'E' 3	56.0	0.0678	2.04	84.9	0.0614	1.820	65.9
Breton Series 'E' 5	28.2	0.1186	1.29	50.5	0.0832	1.530	55.8
Breton Series 'F' 3	83.7	0.0656	1.72	112.4	0.0654	2.490	74.5
Breton Series 'F' 5	58.3	0.0713	1.74	91.2	0.0678	2.440	63.9

No*, K* and S* are estimates of mineralization potential and rate constants and their standard deviations respectively from values of cumulative mineralized N leached.

No, K and S are estimates of mineralization potential and rate constants and their standard deviations respectively from values of total N leached.

In both Saskatchewan and Queensland studies No and k were also estimated by non-linear regression techniques.

Among the virgin soils of the Chernozemic order, No generally increased from Brown to Dark Brown to Black soils in this study. A similar trend was also observed for the cultivated soils. These observations are illustrated in Fig. 3 and Table 6. Losses due to cultivation were generally lower for the less humid Brown than for the more humid Dark Brown and Black Chernozemics. This is probably a reflection of the observation that the greater the initial nitrogen content, the greater the fall when cultivated (Jenkinson,1981). Similar observations have been reported by Campbell and Souster (1982) in Saskatchewan. In the Saskatchewan study however, No was similar among soil zones in the cultivated soils.

Within the Breton plots, No was higher in the non-fallow plots, i.e. series F than in the fallow plots i.e series E. These observations are illustrated in Fig. 3 and Table 7. The effect of fallow is thus similar to the effect of cultivation on virgin soils in the Chernozemic Order. No increased from soil no. 14 to soil no. 13 to soil no. 16 and was highest in soil no. 15. Two reasons could be assigned to this trend. Firstly, the effect of cultivation on soil organic matter varies considerably, probably depending on the organic content of the soil, particularly the amount of the fresh organic matter(Powlson,1980). Fresh residues are thought to be more easily decomposable than the other

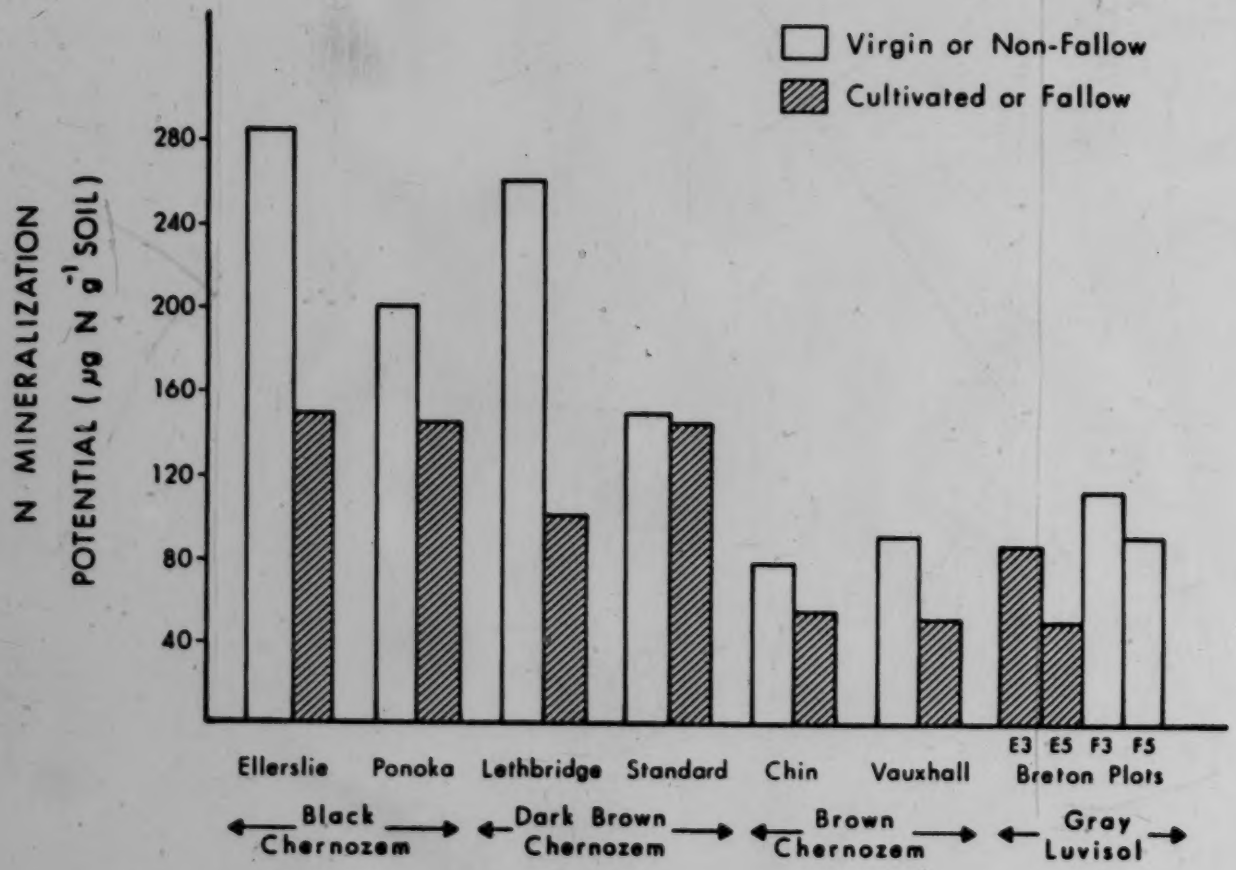

Fig. 3: Comparison of N mineralization potentials in virgin and cultivated soils in the Chernozemic Order, and soils from fallow and non-fallow plots at Breton.

Table 6: Effect of Soil Zone and cultivation on Total N, N mineralization potential(No), active fraction(No/Total N) and mineralization rate constant(k) in Chernozemic soils.

Soil Type and Great Group	Total N ug/g soil		No ug/g soil		No/Total N (%)		k week^{-1}	
	V	C	V	C	V	C	V	C
Black								
Ellerslie	7928.1	5267.5	285.7	147.1	3.6	2.8	0.0584	0.061
Ponoka	2617.3	3386.6	201.6	142.6	7.7	4.2	0.0414	0.063
Mean	5272.5	4327.1	216.4	145.4	5.7	3.5	0.0499	0.062
Change(%)*	-17.9		-32.6		-38.6		+24.4	
Dark Brown								
Lethbridge	2503.9	1666.9	240.4	99.9	9.6	6.0	0.0609	0.087
Standard	2651.5	2481.2	150.7	143.0	5.7	5.8	0.0511	0.066
Mean	2577.5	2074.1	195.6	121.5	7.7	5.9	0.0560	0.071
Change(%)*	-19.5		-37.9		-23.3		+37.6	
Brown								
Chin	1781.4	1706.8	77.7	53.9	4.3	3.1	0.0934	0.097
Vauxhall	1849.4	1305.5	89.4	51.3	4.8	3.9	0.0869	0.094
Mean	1815.4	1506.2	83.6	52.6	4.6	3.5	0.0902	0.095
Change(%)	-17.0		-37.1		-23.9		+5.5	

V = Virgin Soil

C = Cultivated Soil

* Decrease or increase due to cultivation. Values are expressed as percentages of the mean differences in total N, No, No/Total N and k between Virgin and cultivated soils.

Table 7: Effect of fallow and fertilizer on Total N,(N) N Mineralization potentiol (No), active fraction, (No/N) and mineralization rate constant (K) in the Breton Plots.

Series and Plot No.	Soil No.	Plot Treatment	Total N ug/g soil	No/N ug/g soil	No (%)	K week^{-1}
E 3	13	Fallow, Fert	1108	84.9	7.7	0.061
E 5	14	Fallow, Unfert	975	50.5	5.2	0.083
F 3	15	Non-fallow, Fert	1721	112.4	6.5	0.066
F 5	16	Non-fallow, Unfert	1539	91.2	5.9	0.068
Change (A)*(%)			-36.1	-33.5	+4.8	+8.6
Change (B)*(%)			+12.5	+39.2	+17.9	-4.2

Change (A) Increase or decrease due to fallowing.

Change (B) Increase or decrease due to fertilizer.

* Values are mean differences expressed as percentages of fallow or non fertilized.

Fert - Fertilizer applied.
Unfert-No fertilizer applied.

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components of organic matter (Campbell,1978). Secondly, much of the N that is being mineralized each year is derived from recycling of old crop residues and from fertilizer N taken up by microbes during the year of application(Campbell et al.,1980). Of the 36 to 60% fertilizer N remaining in soil after one crop of wheat, Juma and Paul(1980) found 30% to be in the biomass which was mineralized with a half life of 2.4 years in the field. The other 70% was in the mineralizable organic N pool with a half life of 7.7 years. Soil no. 15 has the highest total N content and the highest No value because of the nature of the rotation and fertilizer additions. Consequently, it would probably contain more fresh and old residues than the other Breton plots. Summerfallowing as practised on series E contributed significantly to the lower values of total N and No found there than series F. Simulations of crop sequences have shown that steady state soil organic matter is affected by the nature of the rotation(Russell, 1981). In Australia, steady state organic matter level was lowest for a wheat-fallow rotation than other cropping practices(Russell and Williams, 1982).

Active Fraction Content

The ratio of mineralization potential,No, to total N present, i.e. No/N is referred to here as the active fraction of soil organic N. The active fraction was first proposed by Jansson(1958) and is frequently used to

designate the portion that gives rise to the greatest proportion of mineralized nutrients in the soil (Allison,1973; Greenland,1971; Khan,1971; Campbell,1978).

In the present study No/N ranged from 2.7 to 9.6%(Tables 6 and 7). This is lower than 7.6 to 28.0% calculated from data of Stanford and Smith(1972), 8.0 to 21.0% reported by Campbell et al.(1981) and 3.8 to 20.5% found by Campbell and Souster(1982). In their studies No was estimated at incubation temperatures of 35°C(Stanford and Smith,1972; Campbell and Souster,1982) and 40°C(Campbell et al.(1982) whereas 22 to 25°C was used in the present study. It has been assumed that No is unaffected by temperature(Stanford et al.,1973; Campbell et al.,1981). This assumption has not however been tested to ascertain its validity. Microbial biomass is an important source of labile N(Jenkinson,1981). Accumulation of mineral N(Monreal and McGill,1981) and estimates of N mineralization potentials(Carter and Rennie,1982) have been found to be closely related to both the initial microbial biomass N and the decrease in size of the latter during mineralization. Jenkinson(1981), quoting results from earlier work by Jenson(1936), showed that the amount of straw C mineralized increased with temperature, although the amount of bacterial biomass tissue remaining in the soil decreased. These reports indicate that higher temperatures used for incubation may tend to overestimate No, due to decreases in microbial tissue during the period of incubation. The

effects will be more significant in soils from areas where microbes are adapted to lower temperatures in the field than those used for incubation. This might explain the lower No/N ratio of the soils used in the present study compared to those from other areas especially Saskatchewan with similar climatic conditions to Alberta, but where incubation experiments were conducted at higher temperatures.

The fraction of total N that was active was generally higher in the virgin soils than the cultivated soils within the Chernozemic Order (Table 6). This is consistent with the view that cultivation causes a decline not only in the total organic matter but also in the proportion which decomposes during incubation(Craswell and Waring,1972). Similar findings have been reported in Saskatchewan(Campbell and Souster,1982). Within both the virgin and cultivated soils, active fraction was highest in the Dark Brown soils(Table 6). By contrast Campbell and Souster(1982) observed that active fraction was highest in the Brown soils from Saskatchewan, and attributed this to probably the more 'preserved' organic matter in the Brown soils due to the more droughty growing seasons that are customary in southwestern Saskatchewan. Soils of similar texture within the three soil zones were used in the Saskatchewan study. In this study, where there were textural differences among the three soil zones, the effect of this factor would appear to be more significant than the effect of climatic changes on active fraction contents. A positive, significant

correlation was observed between clay content and No(Table 8). Percentage clay content was highest in the Dark Brown soils (Table 1). Jenkinson(1977) showed that on incubation, more labelled added C was retained by a soil with a clay content of 18% than one with a clay content of 8%. Craswell and Waring(1972), have also shown that clay soils, particularly those with expanding lattice clays, release some decomposable organic matter when ground. The effect of clay in stabilizing organic matter and protecting it from decomposition is well documented.

In contrast to the effect of cultivation which decreased No/N ratios in Chernozemic soil soil samples, fallow tended to increase No/N ratio in the soil samples from the Breton plots on Luvisolic soils(Table 7).

These apparently contradictory observations from the two groups of soils could be related to differences in proximity of the cultivated soils to their respective steady states(McGill,1983). An accurate assessment cannot be made of the exact period of cultivation of all the soils used. The Breton plots have however been under controlled cultivation for about 50 years.

Cultivation causes degradation of soils leading to more rapid initial removal of the potentially mineralizable N, No, than total N Therefore No approaches steady state conditions faster than total N. The rate of this approach will be increased by summerfallow practices. As steady state conditions are approached, declines in rate of No loss will

Table 8: Correlation coefficients between No or No/Total N and particle size fractions in soils.

	No	No/Total N
Clay	0.36**	0.04
Silt	-0.13	-0.08
Sand	-0.23**	-0.01

**--Indicates significance at the 1% level of probability.

be greater than declines in rate of total N loss. Once No reaches steady state it forms an increasing proportion of the total N in a degrading system and a decreasing proportion of the total in a system accumulating organic matter(McGill, 1983). Series E of the Breton plots probably depicts the former situation while the latter situation is exemplified by series F(Table 7).

Chernozemic soils are generally degraded at slower rates than Luvisolic soils. The Chernozemic soils used in this study here are therefore probably in a degrading phase with No not close to steady state conditions. Thus the cultivated soils have lower No/N ratios than their corresponding virgin soils and the soil samples from the Breton plots(Tables 6 and 7). Further examples of above trends are found in data of Campbell and Souster(1982). They reported higher No/N ratios in cultivated than virgin soil samples from the Luvisolic order. The converse was true in soil samples from the Chernozemic Order. Their data also showed mean No/N ratios in cultivated samples from three soil zones of the Chernozemic order were all lower than those found in the cultivated Luvisolic soil samples.

The active fraction was larger in the fertilized plots than the non-fertilized plots in this study. Mineralizable N accumulated at a faster rate than total N in the former plots than in the latter plots(Table 7). These observations are consistent with the finding by Juma and Paul(1980) that 30 and 70% of the fertilizer N remaining in the soil after

one crop of wheat, was in the microbial biomass and the mineralizable non-biomass pools respectively. The effect of fertilizer on the active fraction was more marked in the fallow plots than in the non fallow plots. This could be attributed to relatively greater increases in total N in the non-fallow plots than the fallow plots. In addition soil samples from fallow plots are closer to steady state conditions and will lose No at slower rates than soil samples from the non-fallow plots.

Relation of No and Active Fraction to Soil properties

Significant and close correlations were observed among No, total N and total C. A significant but less close correlation was also observed between No and C/N ratio(Table 9). These are to be expected because a close correspondence had been shown between C and N cycling through soil organic matter(McGill et al.,1975), and Swift(1976) observed that elemental ratios were of little value in predicting rates of mineralization. Other observations in the literature are consistent with these findings (Stanford and Smith,1972; Mario et al.,1980; Campbell et al.,1981). Negative correlations were observed between No/N ratios and total N and total C but these were poor. Cation exchange was also negatively and poorly correlated with the active fraction(Table 9). Similar observations were also noted with data of Stanford and Smith (1972). These are shown in Table 10. In contrast Campbell et al.(1981) found that the No/N

Table 9: Correlation coefficients between No, k or No/Total N and total C, total N, C/N ratio or CEC.

	No	No/Total N	k
C	0.77**	-0.34**	-0.44**
N	0.76**	-0.35**	-0.41**
C/N	0.33**		-0.27**
CEC	0.61**	-0.19*	-0.044**
No		0.29**	-0.68**

* Indicates significance at 5% level of probability.
** Indicates significance at 1% level of probability.

Table 10: Correlation coefficients between No, k at 40°C No/Total N versus and C, total N or CEC calculated from data of Stanford and Smith(1972). No was estimated by Talpaz et al(1981).

	No	No/Total N	k
C	0.76**	-0.35**	-0.20*
N	0.84**	-0.36**	-0.18*
CEC	0.59**	-0.26**	-0.23**
No		0.07	-0.22**

** Indicates significance at 1% level of probability.
* Indicates significance at 5% level of probability.

ratio was not correlated with organic matter content but was positively correlated with cation exchange capacity and they attributed this to adsorption and protection by expanding lattice clays of aliphatic nitrogen and nitrogen of microbial origin. Craswell and Waring(1972) also observed that considerable amounts of organic matter, resistant to decomposition until soils are physically disrupted, exist in soils. It may be expected therefore that a higher proportion of organic matter in coarser textured soils would be more exposed to decomposition than that occurring in finer textured soils.

Further statistical analyses, however, failed to show any correlation between any particle size fraction and the active fraction. In contrast, a positive significant correlation has been observed between the clay fraction and No(Table 8). These observations indicate that correlations between No and texture may provide a better assessment of the theory that expanding lattice clays adsorb and protect aliphatic nitrogen and nitrogen of microbial origin against rapid decomposition than the correlation between active fraction and cation exchange capacity as proposed by Campbell et al.(1981). Further substantiation is provided by the positive correlations found between No and cation exchange capacity in this study(Table 9) and data of Stanford and Smith(Table 10). Correlations between No/N ratios and CEC were poor in both studies.

Nitrogen Mineralization Rate Constant

Rate of mineralization may be defined as amount of the mineralizable pool of N being decomposed per unit time(eg. 1 week),that is(No -Nt)/t. Another method is to express it as fraction being removed per unit time. Such a fractional loss is known as a rate constant and is represented by 'k' in the literature,i.e. a constant fraction disappears in consecutive intervals of time. Thus, the amount lost in a given time is proportional to the amount of mineralizable N at the beginning of the time span. A general expression for estimation of such fractional loss was given by Shipley and Clark(1972)

i.e. estimate of $k=[(No-Nt)/No]/t$

The symbol No is the amount of mineralizable N at the beginning of the time span and Nt is the amount observed later at time t. From the above equation therefore $No.k=No-N/t$,i.e. the product of No and k is the amount of potentially mineralizable N in a time span (e.g. 1 week). Values of k in this study were however obtained using the integrated form of the above equation,i.e. $Nt=Noexp(-kt)$.

Nitrogen mineralization rate constants estimated in this study ranged from 0.041 to 0.097 $week^{-1}$ with an average of 0.069 $week^{-1}$(Table 5). This denotes that at 22°C the potentially mineralizable N(No) is released at an average rate of 6.9% per week, based on the quantity of mineralizable N remaining after each succeeding week of incubation(No - Nt). Within the Chernozemic soils k values

were highest in the Brown soils and least in the Black soils. This was true for both virgin and cultivated soils(Table 6). The k values for the latter soils were however higher than those for the former soils. Fractional losses of No per week were therefore highest in the Brown soils and least in the Black soils, and higher in the cultivated soils than in the virgin soils. The differences between the cultivated soils and virgin soils reflect either a change in the suite of materials within the No pool or a change in mode of stabilization of the No due to cultivation.

Differences in k values of the Chernozemic soils might be due to differences in the nature of organic matter occurring in the three soil zones. In an aggrading sequence of soils, the Brown soils are thought to be less mature than the Dark Brown and Black soils(McGill and Cole,1981). Less stable organic matter will thus appear to exist in the Brown soils than in the soils from the other zones. Consequently its potentially mineralizable N, No, will be more labile resulting in greater fractional losses than in the Dark Brown and Black soils when incubated under similar conditions. [2] These observations seem to support findings by Cassman and Munns (1980) and Campbell et al.(1981) that k values for subsoils were higher than those for surface soils.

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[2]McGill W. B., personal communication

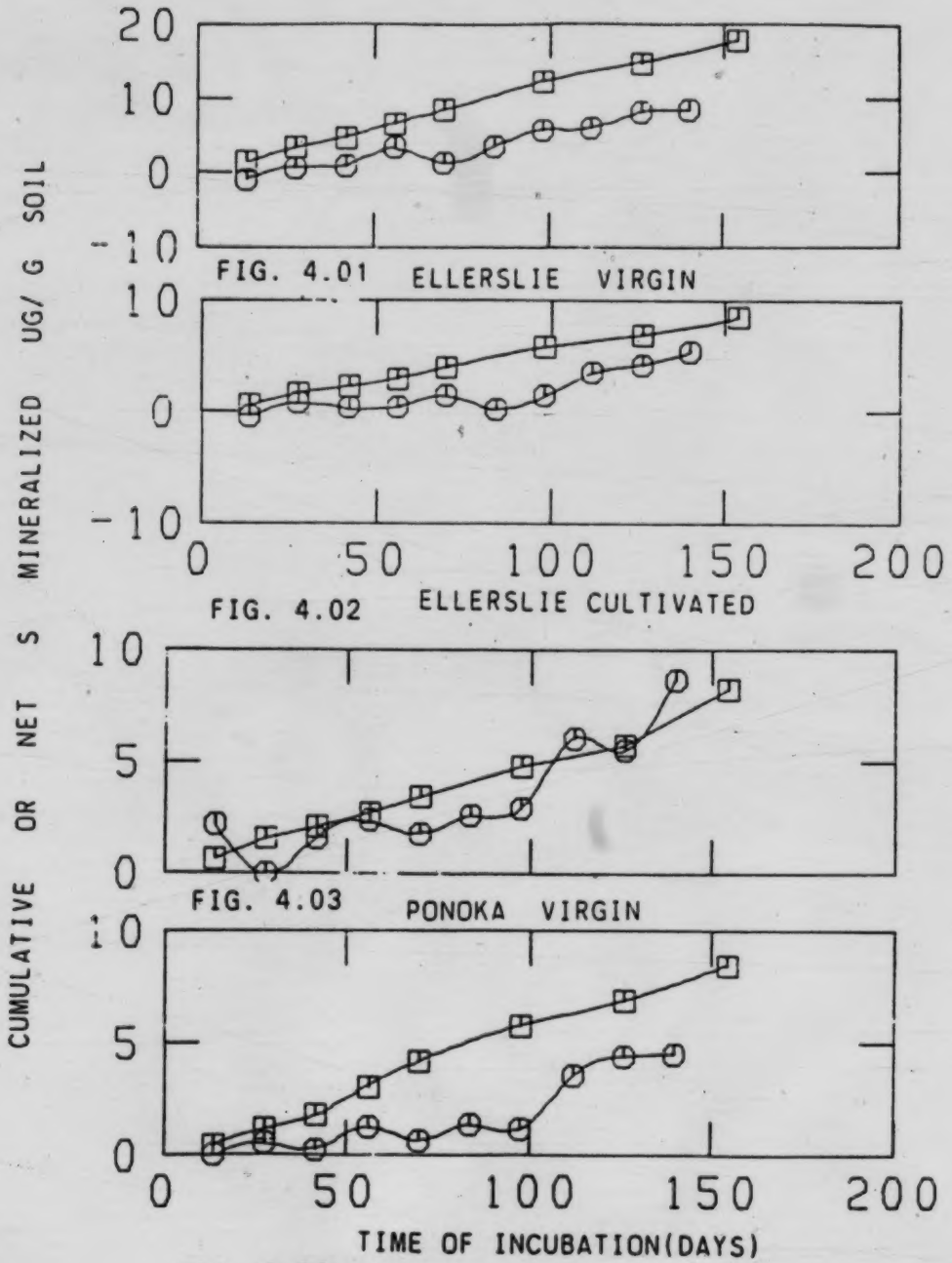
In the soil samples from the Breton plots, mean k value was higher in those from the fallow plots(0.072 week^{-1}) than those from the non-fallow plots(0.067 week^{-1})(Table 7). This may be attributed to faster decomposition rates due to better aeration conditions and the release of locked up labile organic matter following frequent tillage practices during summerfallowing.

There were no consistent relationships between k values found in the cultivated soil samples from the Chernozemic Order and those from the Breton plots. Overall mean k value(0.076 week^{-1}) for the Chernozemic cultivated soil samples was higher than the mean k value(0.070 week^{-1}) for the Breton plots.

B. SULPHUR

S Mineralization Time Curves

Figs. 4.01 to 4.16 illustrate the S mineralization time curves obtained using the two methods of incubation. S mineralization curves with method 1, i.e.continuous incubation, were irregular with time. A similar trend was observed with nitrogen. Mineralization curves of other workers(eg. Kowalenko and Lowe,1975) have been observed to display irregularity with time during continuous incubation. This might be due to cumulative inhibitory effects on mineralization arising during continuous incubation in



Figs. 4.01, 4.02, 4.03 and 4.04 represent cumulative or net amounts of S mineralized in above soils with time of incubation.

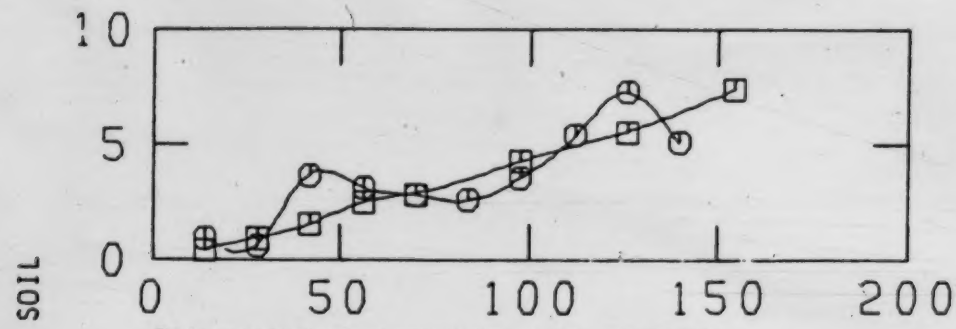


FIG. 4.05 LETHBRIDGE CULTIVATED

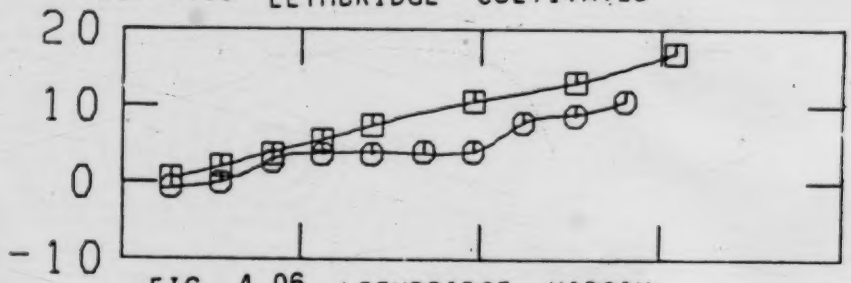


FIG. 4.06 LETHBRIDGE VIRGIN

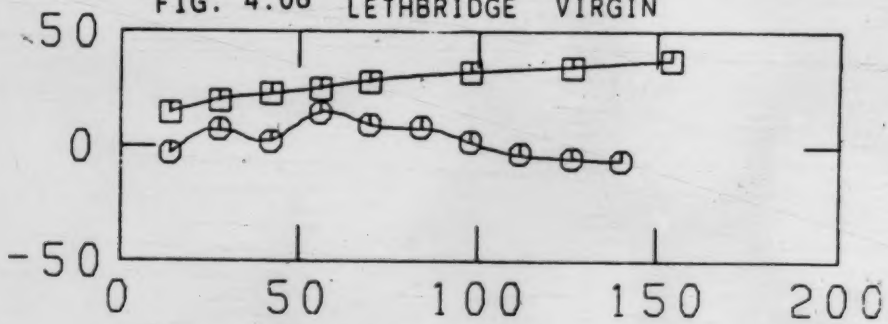


FIG. 4.07 STANDARD CULTIVATED

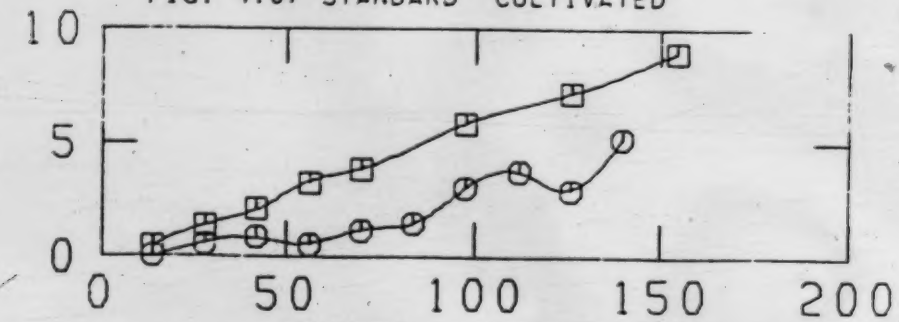


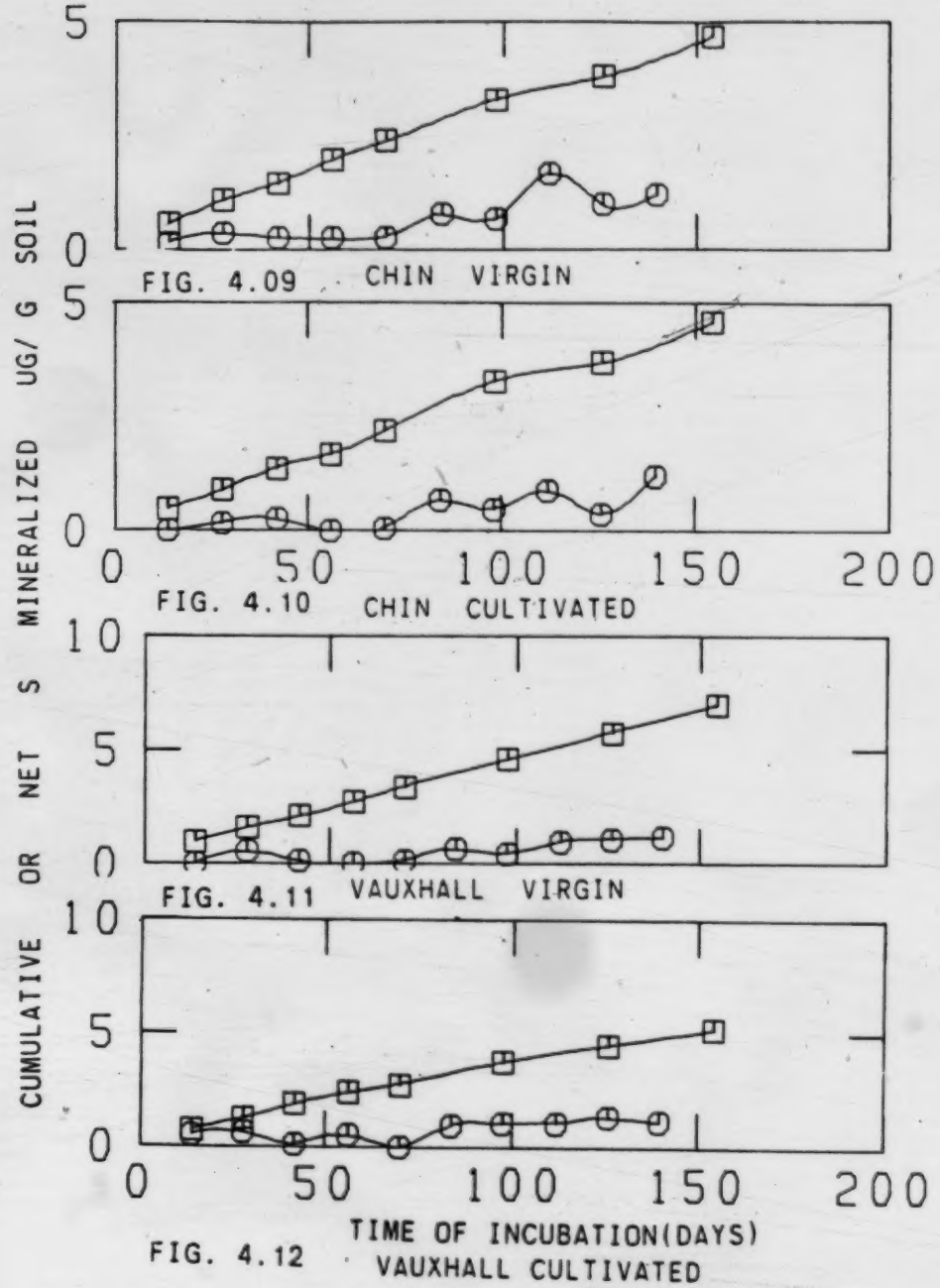
FIG. 4.08 STANDARD VIRGIN

CUMULATIVE OR NET S MINERALIZED UG/ G SOIL

Figs. 4.05, 4.06, 4.07 and 4.08 represent cumulative or net amounts of S mineralized in above soils with time of incubation.

CONTINUOUS INCUBATION(NET S)

INCUBATION AND LEACHING(CUMULATIVE S)



Figs. 4.09, 4.10, 4.11 and 4.12 represent cumulative or net amounts of S mineralized in above soils with time of incubation.

CONTINUOUS INCUBATION(NET S) - —⊖—⊖

INCUBATION AND LEACHING(CUMULATIVE S) - —⊡—⊡

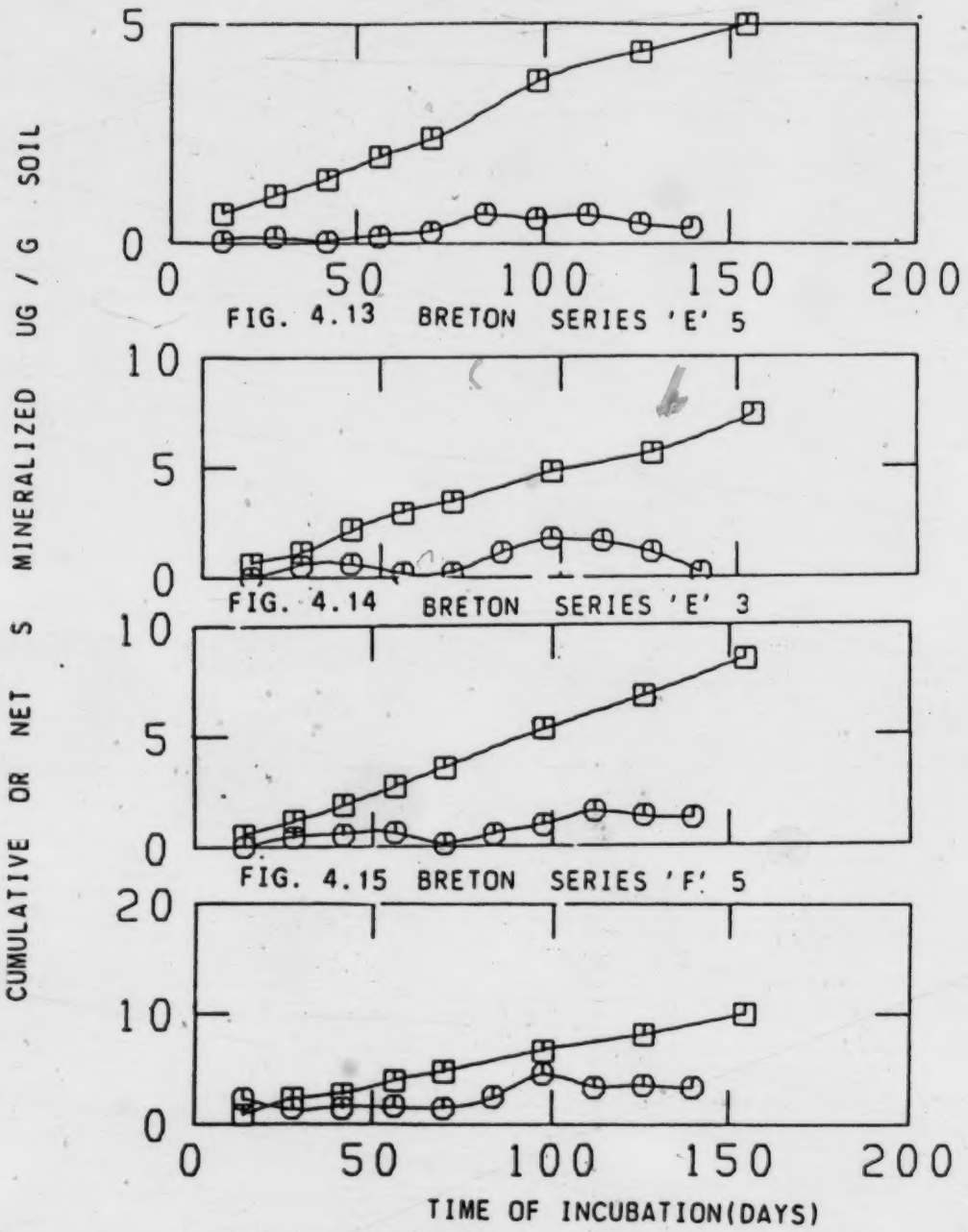


FIG. 4.13 BRETON SERIES 'E' 5

FIG. 4.14 BRETON SERIES 'E' 3

FIG. 4.15 BRETON SERIES 'F' 5

FIG. 4.16 BRETON SERIES 'F' 3

Figs. 4.13, 4.14, 4.15 and 4.16 represent cumulative or net amounts of S mineralized in above soils with time of incubation.

CONTINUOUS INCUBATION(NET S) —

INCUBATION AND LEACHING(CUMULATIVE S) —

flasks as was suggested by Stanford and Smith(1972). Another factor might be fluctuations in rates of oxygen supplied due to the method of mixing used to achieve uniformity in moisture distribution. Though these observations were made in respect of N, similar explanations would be applicable to S. This may be more relevant in situations such as S deficient soils where arylsulfohydrolases may have a major role in S mineralization. Arylsulfohydrolases are subject to end product inhibition (Fitzgerald,1978) and Kowalenko and Lowe(1975) observed that arylsufolhydrolase activity declined sharply in all four soils they studied throughout a 14 week incubation. Kowalenko and Lowe's study was done in the absence of plants, therefore the extracted sulphate may not have been the same as the mineralized S that could taken up by plants(Speir, 1977).

Limited information is available on S mineralization using method 2, i.e.incubation and leaching. Cumulative S mineralized was almost linear with time in all soils (Figs. 4.10 to 4.25). Tabatabai and Al-Khafaji(1980) also observed that cumulative S mineralized was linear with time in the 12 soils they worked with in Iowa.

The equation describing N mineralization rate with time cannot be applied to S mineralization because cumulative S mineralized was more linear than curvilinear to time of incubation, i.e. amount of S mineralized appears not to be dependent on substrate concentration. A maximum value, i.e. S mineralization potential, cannot therefore be estimated.

Data were subjected to analysis by linear regression. Table 11 shows the intercepts, slopes(rates) and the correlation coefficients of the equations describing the linear relationship between cumulative S mineralized and time of incubation.

Cumulative S Mineralized and Rate of S Mineralization

With the exception of the soils from the Standard site, cumulative S mineralized was higher in the virgin soils than the cultivated soils within the Chernozemic Order(Table 12). The lowest amount of cumulative S mineralized were found in the Brown soils, at both the virgin and cultivated site. Expressed as percentages of total S, cumulative amounts of S mineralized ranged from 1.2 to 3.0% in the virgin soils and 1.1. to 1.8% in the cultivated soils excluding soil no. 8.,i.e. Standard cultivated. The percentage of total S mineralized was also lowest in the Brown soils.

The lower percentages of total S mineralized upon cultivation is consistent with earlier observations that cultivation causes a decline not only in the total organic matter but also in the proportion of organic matter which decomposes during incubation (Craswell and Waring,1972). Differences in rate of mineralization due to cultivataion were however lowest in the Brown soils. This is a reflection of differences in cumulative S mineralized between virgin and cultivated soils in the three soils. Table 12, shows that this difference was lowest in the Brown Soils. The

Table 11: Parameters and correlation coefficients of linear relationships between cumulative S mineralized and time.

Soil Type	Slope	Intercept	Correlation Coefficient
Ellerslie Virgin	0.82	0.14	0.9987
Ellerslie Cultivated	0.35	-0.02	0.9934
Ponoka Virgin	0.40	-0.29	0.9953
Ponoka Cultivated	0.39	-0.01	0.9964
Lethbridge Virgin	0.80	-0.89	0.9989
Lethbridge Cultivated	0.34	-0.35	0.9976
Standard Virgin	0.42	-0.29	0.9987
Standard Cultivated	1.07	15.89	0.9724
Chin Virgin	0.20	0.31	0.9973
Chin Cultivated	0.20	0.12	0.9960
Vauxhall Virgin	0.30	0.35	0.9997
Vauxhall Cultivated	0.22	0.54	0.9943
Breton Series 'E' 3	0.32	0.13	0.9964
Breton Series 'E' 5	0.22	0.22	0.9953
Breton Series 'F' 3	0.45	0.30	0.9982
Breton Series 'F' 5	0.40	-0.039	0.9993

Table 12: Effect of soil zone and cultivation on total S, cumulative S mineralized, rates of S mineralization and percentage of S mineralized.

Great Group and Soil Location	Total S (ug S/g soil)		Cumulative Mineralized S(ug S/g soil)		Rate of Mineralization (ug S/g soil Week^{-1})		Cumulative S Mineralized /Total S (%)	
	V	C	V	C	V	C	V	C
Black								
Ellerslie	1187.0	732.5	17.9	8.2	0.82	0.35	1.5	1.1
Ponoka	397.2	472.9	8.5	8.5	0.40	0.39	2.1	1.8
Mean	792.1	602.7	13.2	8.4	0.61	0.37	1.8	1.5
*Change Due to Cultivation (%)	-23.9		-36.3		-39.3		-16.6	
Dark Brown								
Lethbridge	566.4	484.4	17.0	7.4	0.80	0.34	3.0	1.5
Standard	504.1	721.1	9.0	37.6	0.42	1.70	1.8	5.2
Mean	535.3	602.8	13.0	22.5	0.61	1.02	2.4	3.4
*Change Due to Cultivation (%)	+12.6		+73.1		+67.2		+41.6	
Brown								
Chin	380.8	392.3	4.7	4.6	0.20	0.20	1.2	1.2
Vauxhall	360.5	400.5	7.0	5.2	0.30	0.22	1.9	1.3
Mean	370.7	396.4	5.9	4.9	0.25	0.21	1.6	1.3
*Change Due to Cultivation (%)	+ 6.9		-16.9		-16.0		-18.8	

* Values are expressed as percentages of the mean differences in total S, cumulative mineralized S, rate of mineralization and % total S mineralized between virgin and cultivated soils.

V = virgin

C = cultivated

Brown soils as shown in Table 1, contain the lowest amounts of organic matter. Total S in both cultivated and virgin soils were similar, while clear marked differences were observed in soil samples from the other soil zones. The least difference in cumulative S mineralized between virgin and cultivated Brown soils is probably a reflection of this trend. Tabatabai and Al-Khafaji(1980) reported higher rates of S mineralization(0.5 to 1.2 ug S g^{-1} soil $week^{-1}$) and higher percentages of total S mineralized (3.5 to 13.3%) at 20°C during a 26 week incubation study in Iowa. The differences in the two studies could probably be due to differences in mineralizable pool of organic S in the soils from the two areas of study.

In the soils from the Breton plots, cumulative amounts of S mineralized were higher both in the non-fallow and fertilized plots than the fallow and non-fertilized plots(Table 13). These are reflections of decreases in total S contents in the latter plots compared to the former plots.

Within the individual plots however, percentage of total S mineralized was higher in soil sample from Breton plot no.'E' 3 than those from the other plots. A similar finding was observed with active fractions of nitrogen. This is due to a higher proportional decrease in total S content than cumulative S mineralized under fallow.

Table 13: Effect of fallow and fertilizer on Total S, Cumulative S mineralized, % of total S mineralized and Rates of mineralization (Rate) in the Breton Plots.

Series and Plot No.	Soil No.	Plot Treatment	Total S ug/g soil	Cum. S ug/g soil	Rate x week^{-1}	Cum. S/Total S %
E 3	13	Fallow, Fert	173	7.4	0.32	4.2
E 5	14	Fallow, Unfert	152	5.0	0.22	3.3
F 3	15	Non-fallow, Fert	252	10.1	0.45	4.0
F 5	16	Non fallow, Unfert	211	8.5	0.43	4.0
Change (A)*(%)			42.6	50.0	59.2	5.0
Change (B)*(%)			17.2	31.3	25.8	10.8

Change (A) Increase due to non-fallowing.

Change (B) Increase due to fertilizer.

* Values are mean differences expressed as percentages of fallow and non fertilized.

Unfert- No fertilizer applied.
Fert - Fertilizer applied.
Cum. S- Cumulative S mineralized
x ----ug S/g soil

Relationship between Cumulative S Mineralized and Soil Properties

Cumulative S mineralized was significantly but poorly correlated with total C and total N. Correlations between cumulative S mineralized and total S, C-bonded S or ester sulphates were about 0.5 and highly significant(Table 3). There was a slight negative correlation with C/S. Tabatabai and Al-Khafaji (1980) did not find any correlation between cumulative amounts of S mineralized and total S. In this study, similar degree of correlation between the two forms of organic S and cumulative S mineralized is of significance. Freney et al. (1975) observed that both fractions contributed available sulphur for plant uptake, and neither of them is likely to be of any value for predicting the sulphur supply of plants.

Relative Kinetics of N and S Mineralization

The rate of mineralization of N decreased with time in all soils, whereas that of S was generally constant from results using the incubation and leaching technique(Figs. 5.01 to 5.16). In contrast, Tabatabai and Al-Khafaji (1980) found that cumulative amounts of both N and S mineralized were linear with time. The decline in N mineralization rate with time would be enhanced by the leaching of potentially mineralizable N during the period of incubation. Leaching of readily mineralizable N should lower subsequent values for N mineralization (Smith et al., 1980). It is however doubtful

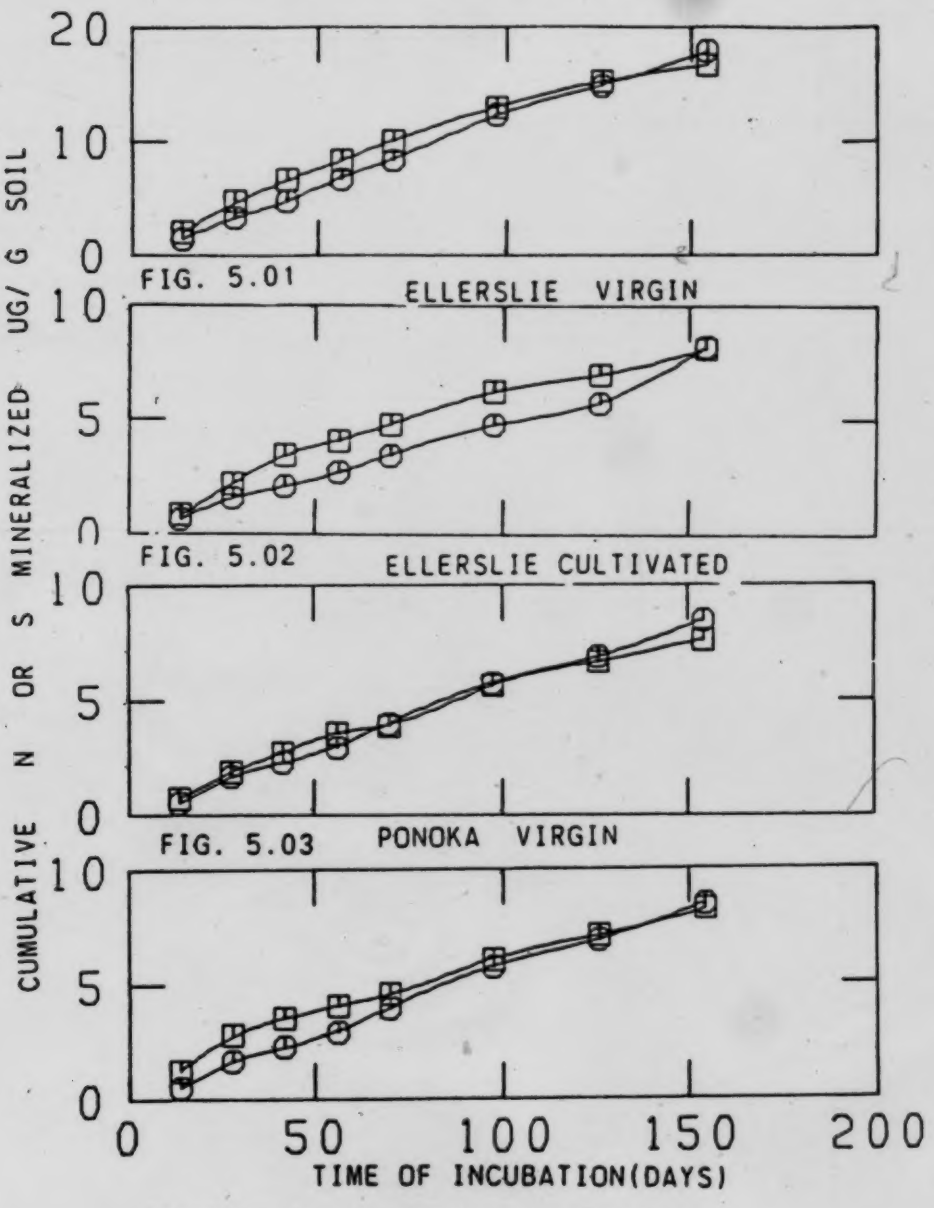


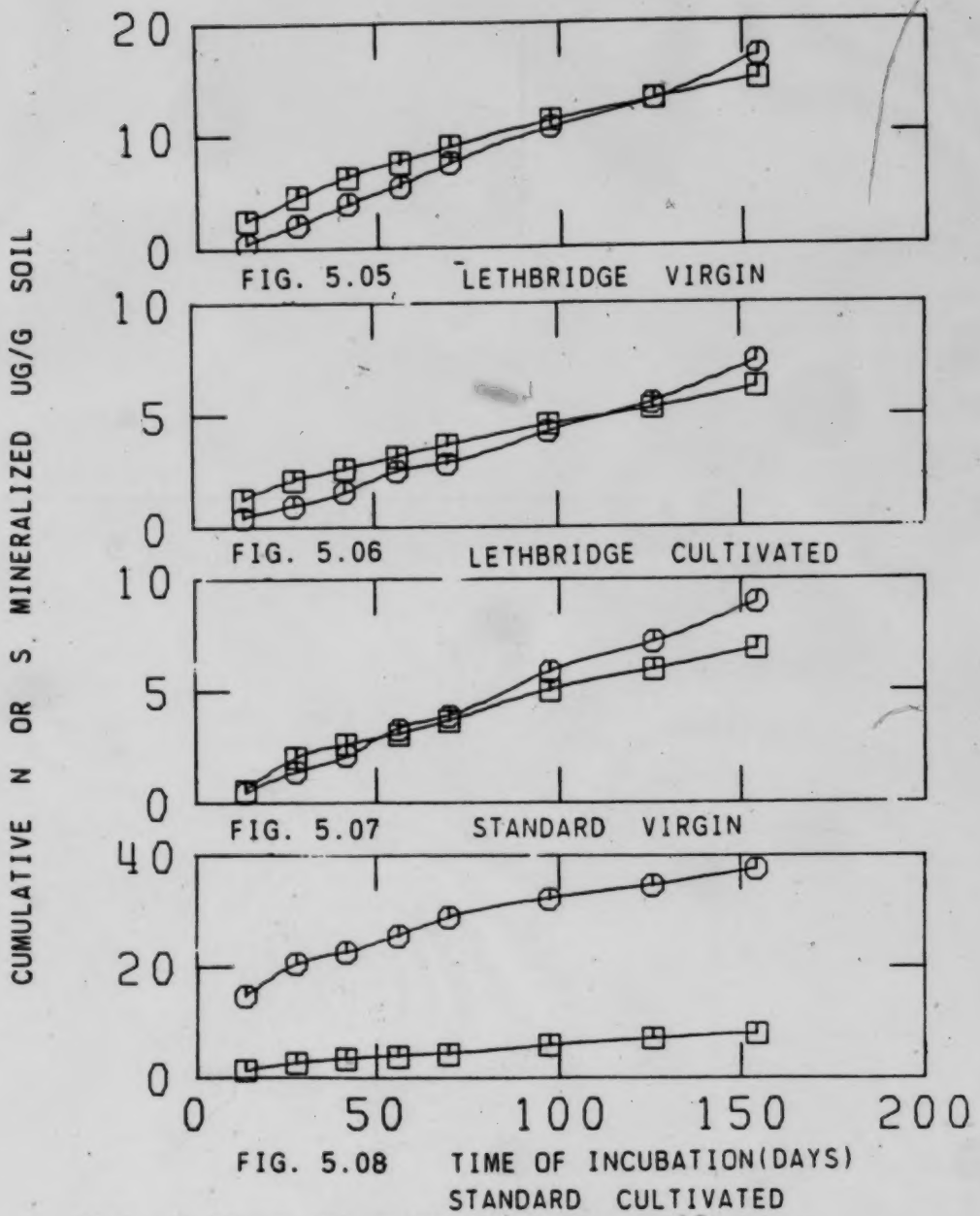
FIG. 5.04 PONOKA CULTIVATED

Figs. 5.01, 5.02, 5.03 and 5.04 represent cumulative amounts of N or S mineralized in above soils with time of incubation.

SCALE

S — 1

N — 1 X 10



Figs. 5.05, 5.06, 5.07 and 5.08 represent cumulative amounts of N or S mineralized in above soils with time of incubation.

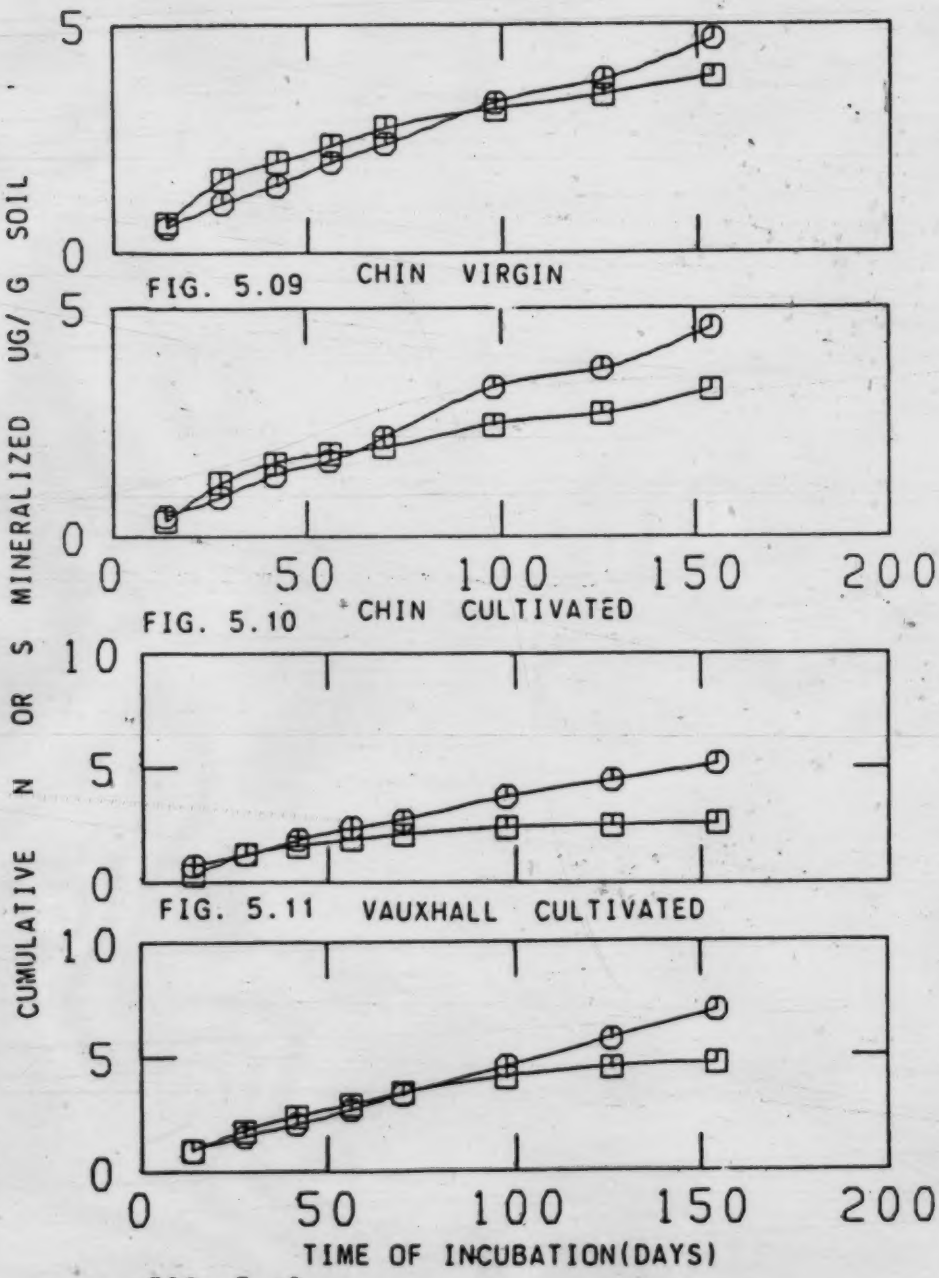


FIG. 5.09 CHIN VIRGIN

FIG. 5.10 CHIN CULTIVATED

FIG. 5.11 VAUXHALL CULTIVATED

FIG. 5.12 VAUXHALL VIRGIN

Figs. 5.09, 5.10, 5.11 and 5.12 represent cumulative amounts of N or S mineralized in above soils with time of incubation.

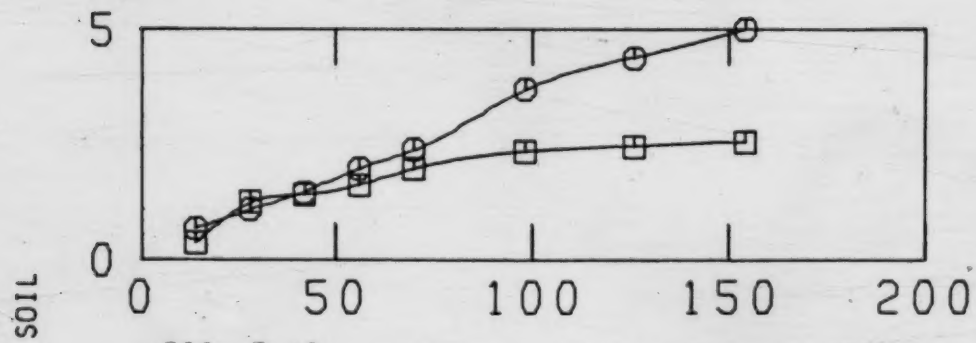


FIG. 5.13 BRETON SERIES 'E' 5

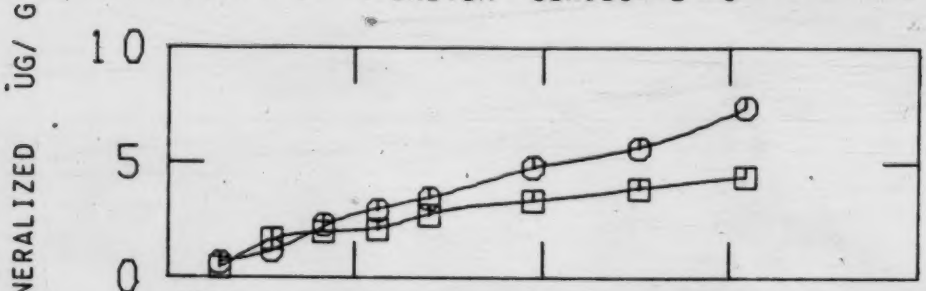


FIG. 5.14 BRETON SERIES 'E' 3

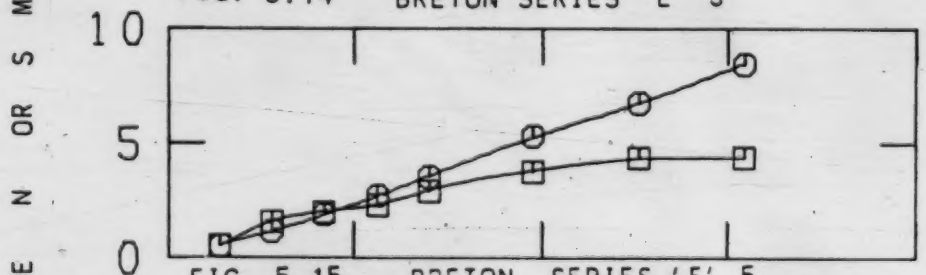


FIG. 5.15 BRETON SERIES 'F' 5

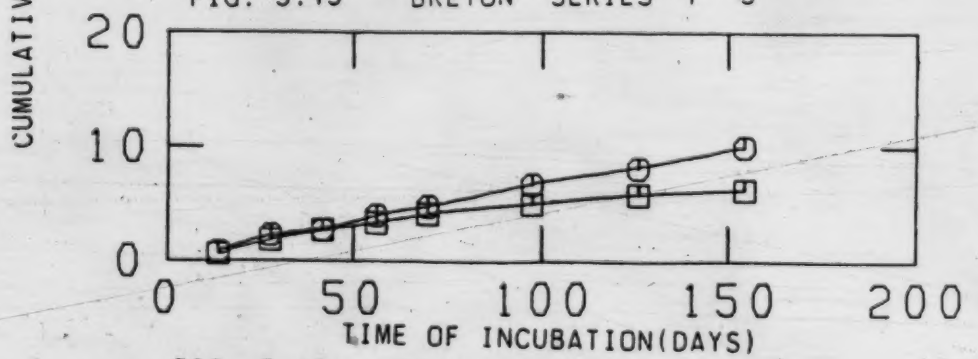
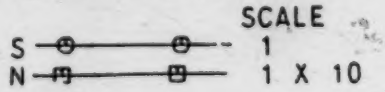


FIG. 5.16 BRETON SERIES 'F' 3

Figs. 5.13, 5.14, 5.15 and 5.16 represent cumulative amounts of N or S mineralized in above soils with time of incubation.



if leaching of organic S reduced the measured amount of S mineralized. The Johnson and Nishita method used for SO_4^{-2} analysis does not differentiate between inorganic SO_4^{-2} and ester sulphates(Freney, 1958), and therefore if any of the latter form of S had been leached out, higher values of S would have been found in the leachates. Though no attempts were made to determine if any amount of C-bonded S was leached out, on the basis of its greater stability than ester sulphate (Bettany et al., 1978; Lowe and DeLong, 1963; Scott and Anderson, 1976), it might be speculated that it will be more resistant to leaching than the sulfate esters. Furthermore, S contents of leachates analysed by ion-chromatography were similar to those obtained by the Johnson and Nishita method in Saskatchewan.[3]. Tests have shown that two kinds of sulfate esters did not interfere in the determination of SO_4^{-2}-S by an ion chromatographic method(Dick and Tabatabai, 1979). Based on the data in the literature,(Jenny 1941, Stanford and Smith, 1972),it has been commonly assumed that N mineralization reactions follow approximate first order kinetics. First order kinetics described N mineralization in this study. The near constant amount of S mineralized in each time interval suggests that S mineralization rates are independent of amount or concentration of mineralizable organic S. Thus S mineralization rate reaction could be assumed to be a zero order reaction which can be represented as

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[3]McGill, W.B. personal communication

$$-dS/dt=k$$

where S is the concentration of sulphur which is disappearing.

The different order reactions observed with nitrogen and sulphur in respect of their mineralization mechanisms are consistent with many observations in the literature. Biederbeck(1978), after reviewing much of the literature on N and S mineralization concluded, that in contrast to the behaviour of N, the rate and extent of release of plant available S from soil organic matter is not closely governed by major soil characteristics such as organic C, N and S content. Furthermore, Swift and Posner(1971) found that fractionation of humic acid extracted from widely different soils showed that highest amounts of N were in the high molecular weight humic acid fractions, and these decreased considerably with decreasing molecular weight. This change in nitrogen content was due mainly to loss of amino acid nitrogen. By contrast, S contents remained constant throughout the molecular weight range. In their view this indicated that unlike N, the S content of humic acid is not dependent on hydrolysable, S containing amino acids. Swift et al.(1970) earlier postulated that within a given extract, physical and chemical changes occur as a function of decreasing humic acid molecular weights. These changes are the results of long-term humification which can be regarded as a slow oxidative process. Recently, Han and Yoshida(1982) observed a linear relationship between time and amount of

p-nitrophenol released by arylsulfohydrolase. p-nitrophenol is the organic end product formed when p-nitrophenyl sulfate is used as a substrate during assay of arylsulfohydrolase activity(Tabatabai and Bremner, 1970).

Statistical analysis of the present data show that cumulative amounts of S and N mineralized were significantly correlated at the 1% level of probability(r=0.525)(Table 3). Tabatabai and Al-Khafaji(1980) also, found that these two variables were significantly correlated. Since total N and S were closely correlated (r=0.899), the lower correlation found between their cumulative amounts mineralized is a reflection of the differences in their mineralization rates reflecting different stabilization and/or mineralization mechanisms.

In agreement with Tabatabai and Al-Khafaji(1980), ratios of total N and S contents of soils were poorly but significantly correlated at the 1% level of probability with the ratios of cumulative amounts of N:S mineralized (r=0.299)(Table 3). This is to be expected because the rates of S mineralization observed were not dependent on the amount of total S, or the two forms of organic S. In contrast N mineralization rate was dependent on No which was highly correlated with total N in the soils used for this study.

The different kinetics observed for N and S mineralization support earlier conclusions made by Lowe and Kowalenko(1975) that although N and S mineralization have

similarities, they are not parallel metabolic processes, i.e. they do not proceed in similar fashion by releasing amounts of these elements in the proportions that would be predicted by the N:S ratios (Swift,1976).

C. EFFECT OF CLIMATE AND MANAGEMENT ON SOIL ORGANIC MATTER

Changes in management affect soil organic matter in two ways: by altering the annual input of organic matter into the soil and by altering the rate at which organic matter decomposes or is lost. It is usually impossible to separate the two effects in analysing the results of a given change in management(Jenkinson,1981). For example, the decline in organic matter that follows the cultivation and cropping of old grassland is partly caused by the decrease in the annual input of organic matter and partly by an acceleration of the decomposition process caused by mechanical disturbance (Craswell and Waring,1972).

The effect of climate on organic matter is depicted by the sequence of Canadian soils from Brown to Black Chernozems. This sequence can be considered as an aggrading sequence defined by McGill and Cole(1981) as a sequence of soils developed along climatic or topographical gradients in which at steady state, each successive member of the sequence has more organic matter, organic-P, -S, or N than the preceeding member usually due to greater additions than removals. Figs. 6.1 and 6.2 and Table 14 illustrate the effect of both climate and cultivation on virgin soils in an

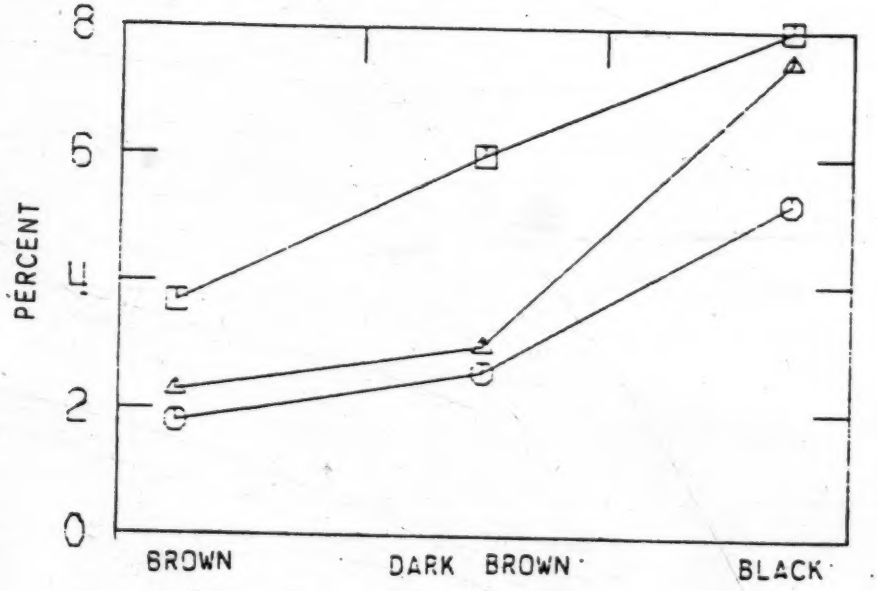

FIG. 6.1

DISTRIBUTION OF TOTAL C, TOTAL N AND TOTAL S AMONG SOIL ZONES OF THE CHERNOZEMIC ORDER (VIRGIN SOILS).

VARIABLE	SCALE
TOTAL C	1
TOTAL N	1 X 10⁻¹
TOTAL S	1 X 10⁻²

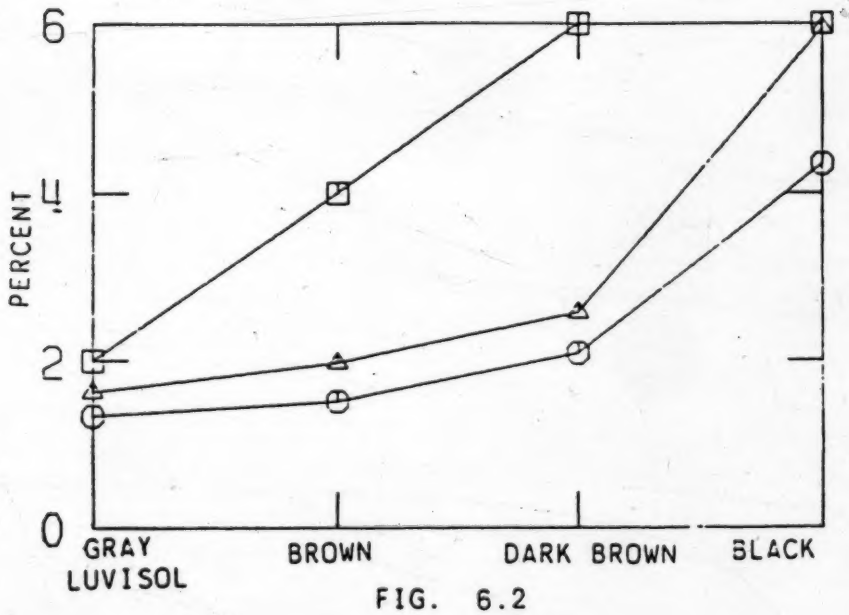

FIG. 6.2

DISTRIBUTION OF TOTAL C, TOTAL N AND TOTAL S AMONG SOIL ZONES OF THE CHERNOZEMIC ORDER (CULTIVATED SOILS) AND SOIL SAMPLES FROM THE BRETON PLOTS(GRAY LUVISOL).

VARIABLE	SCALE
TOTAL C	1
TOTAL N	1 X 10⁻¹
TOTAL S	1 X 10⁻²

Table 14: Effect of cultivation and soil zone on Total C, Total N, Total S, HI-reducible S and C-bonded S.

Great Group and Soil	Total C (%)[1] VN	Total C (%)[1] CF	Total N (%)[1] VN	Total N (%)[1] CF	Total S (%)[1] VN	Total S (%)[1] CF
Black						
Ellerslie	10.77±1.5	6.95±1.0	0.793±2.0	0.527±0.9	0.1187±2.0	0.0733±1.4
Ponoka	4.72±0.2	5.00±0.9	0.262±0.5	0.339±0.7	0.0397±3.0	0.0473±2.1
Mean	7.75	5.98	0.528	0.433	0.0792	0.0600
*Change		-22.8		-17.9		-24.4
Dark Brown						
Lethbridge	2.97±0.2	2.27±0.2	0.250±0.6	0.167±0.9	0.0566±1.2	0.0484±2.0
Standard	3.09±0.2	2.88±0.4	0.265±0.6	0.248±0.9	0.0504±0.7	0.0721±1.2
Mean	3.03	2.58	0.258	0.208	0.0535	0.0603
*Change		-24.7		-24.0		+12.7
Chin	2.25±0.1	2.39±0.2	0.178±1.1	0.171±0.3	0.0381±0.6	0.0392±0.4
Vauxhall	2.41±0.2	1.54±0.1	0.185±0.9	0.131±0.5	0.0360±1.0	0.0400±1.5
Mean	2.33	1.97	0.182	0.151	0.0371	0.0396
*Change		-15.5		-17.0		+6.7
Gray Luvisol (Breton Plots)						
No. 3	2.11±0.2	1.33±0.2	0.172±0.1	0.111±0.4	0.0252±0.2	0.0211±0.2
No. 5	1.99±0.3	1.12±0.4	0.154±0.3	0.095±0.2	0.0173±0.4	0.0152±0.1
Mean	2.05	1.23	0.163	0.103	0.2130	0.0182
*Change (%)		-66.7		-58.2		-42.3

Table 14: (con't)

Great Group and Soil	HI - S (%)[1] VN	HI - S (%)[1] CF	C-bonded S (%)[1] VN	C-bonded S (%)[1] CF
Black				
Ellerslie	0.0893±3.5	0.0579±0.6	0.0294±4.0	0.0154±1.1
Ponoka	0.0267±0.7	0.0371±0.5	0.0131±0.6	0.0102±0.9
Mean	0.0580	0.0480	0.0224	0.0128
*Change		-17.2		-42.9
Dark Brown				
Lethbridge	0.0413±1.6	0.0366±1.1	0.0153±1.7	0.0118±1.4
Standard	0.0338±0.9	0.0523±1.4	0.0169±0.9	0.0198±1.8
Mean	0.0376	0.0445	0.0161	0.0193
*Change		+18.3		+19.8
Chin	0.0242±0.3	0.0219±0.9	0.0139±0.4	0.0174±1.1
Vauxhall	0.0213±0.8	0.0280±0.6	0.0147±0.5	0.0113±0.4
Mean	0.0238	0.0250	0.0143	0.0144
*Change		+9.6		+0.7
Gray Luvisol (Breton Plots)				
No. 3	0.0158±0.6	0.0093±0.4	0.0094±0.6	0.0080±0.3
No. 5	0.0106±0.8	0.0068±3.3	0.0105±1.0	0.0084±0.4
Mean	0.0132	0.0081	0.0081	0.0082
*Change (%)		-39.2		-17.8

* Values are expressed as percentages of mean differences in total C, total N, total S, HI-reducible S and C bonded S between: (i) Virgin and Cultivated soils of the Chernozemic Order and (ii) Non-Fallow and Fallow Plots at Breton.

VN - Virgin Chernozemic soils or Non-Fallow Breton plots.

CF - Cultivated Chernozemic soils or Fallow Breton plots.

Total C[1] - Standard deviations to be multiplied by 10^{-1}.

Total N[1] - Standard deviations to be multiplied by 10^{-1}.

Total S[1], HI-S[1] and C-bonded S[1] - Standard deviations to be multiplied by 10^{-1}.

aggrading sequence of the Chernozemic Order. Total N, total C and total S contents generally increased from Brown to Black soils in both cultivated and virgin soils. Mean values for total N and total C were generally lower in the cultivated soils than the virgin soils. The decline due to cultivation in mean total C and total N followed each other closely in the three soil zones(Table 14). Further proof is offered by examination of elemental ratios(Table 15). Mean C/N ratios of cultivated soils within each soil zone were very similar to C/N ratios of corresponding virgin soils.

The effect of cultivation on total S was rather inconsistent. As the graphs in Figs. 6.1 and 6.2 and values in Table 14 show, mean total S increased in both the Brown and Dark Brown soil zones but decreased in the Black soil zone with cultivation. This might not however be surprising. In Oklahoma and Kansas states it has been observed that some cultivated soils contained as much total S as adjacent virgin soils; and in some few cases the total S content was higher in the sample from the cultivated site. In the latter state, this was mainly on soils that produced alfalfa for several years in the subhumid and semiarid areas(Harper, 1959). Cultivation did not change mean C:N ratios of virgin soils, but narrowed C:S ratios in work done by Swift(1976). Swift(1976), therefore postulated that on average, in the soils he examined C and N accumulated at the same rate in the virgin soils and mineralized at almost equal rates upon cultivation. The lower C:S ratios observed upon cultivation

Table 15: Comparison of elemental ratios of C/N, C/S and N/S in virgin (V) and cultivated (C) soils of the chernozemic order.

	C/N		C/S		N/S	
	V	C	V	C	V	C
Black						
Ellerslie	13.58	13.18	90.70	94.80	6.70	7.20
Ponoka	18.01	14.75	118.90	105.70	6.60	7.20
Mean	15.80	13.80	104.80	100.30	6.70	7.20
Dark Brown						
Lethbridge	11.88	13.59	52.47	46.90	4.42	3.44
Standard	11.66	11.62	61.31	34.94	5.26	3.44
Mean	11.77	12.61	56.89	43.42	4.48	3.44
Brown						
Chin	12.64	13.98	59.06	60.97	4.68	4.35
Vauxhall	13.03	11.76	66.94	38.50	5.13	3.26
Mean	12.84	12.87	63.00	49.74	4.91	3.81
Overall Mean	13.50	13.10	75.00	64.50	5.40	4.80

indicated that S accumulated at lower rates than in the virgin soils and/ or mineralized less rapidly upon cultivation. Similar conclusions can be reached regarding C and N cycling in this study. The generalization made by Swift(1976) regarding C and S cycling relationship will not be extended to results from the Chernozemic soils in this study, because the narrowing of C/S ratios was due as much to a gain of S as a to loss of C. Generally, the observations tend to support the notion of a dichotomy between cycling of C and N on one hand and of S on the other(McGill and Cole,1981). Effects of management practices are explicitly illustrated in the soil samples from the Breton plots (Tables 14 and 16). Organic matter contents were generally higher in the non-fallowed and fertilized plots than the fallowed and non-fertilized plots respectively. The net rate of turnover of organic matter is faster in fallowed land than in land being cropped(Shields and Paul,1973; Fehr and Sauerback,1968; Martel and Paul,1974; Campbell and Paul,1978).

Relationships between C,N and S in these plots bear further testimony to the idea of dichotomy between cycling of C and N on one hand and of S on the other. Increases in total C and total N due to non-fallowing followed each other closely with increases in total S falling behind(Tables 14 and 16) Examination of elemental ratios reveals further the intimate relationship between C and N and the non intimate relationship between C and S. Mean C:N ratios in fallow

Table 16: Effect of fallow and fertilizer on total C, total N and total S contents in the Breton plots.

Series and Plot No.	Soil No.	Plot Treatment	Total C %	Total N %	Total S %
E 3	13	Fallow, Fert	1.33	0.111	0.0173
E 5	14	Fallow	1.12	0.095	0.0152
F 3	15	Non-fallow, Fert	2.11	0.172	0.0252
F 5	16	Non fallow	1.99	0.154	0.0211
Change (A)*(%)			66.7	58.3	42.3
Change (B)*(%)			10.6	12.5	17.0

Change (A) Increase due to not fallowing.

Change (B) Increase due to fertilizer.

* Values are expressed as percentages of mean differences in Total C, Total N and Total S between: (i) non-fallow plots (F3 and F5) and fallow plots (E3 and E5) and (ii) fertilized plots (E3 and F3) and non-fertilized plots (E5 and F5).

Fert - Fertilizer.

plots were slightly lower than in the non-fallow plots while C:S ratios were remarkably lower in the former plots than the latter(Table 17). This corroborates the observation made by Swift(1976) that during mineralization or accumulation of organic matter N follows C more closely than S. Jenkinson(1981) also noted that when an old cropped soil was left uncultivated C and N accumulated at similar rates. The slight decrease in C:N ratios with summerfallowing could be attributed to recycling of nitrogen in soils(Martel and Paul,1974). Carbon is decomposed to CO_2 during decomposition, whereas the nitrogen is mineralized and some of it is re-used by microorganisms. On this basis, Martel and Paul(1974) suggested that 10% of the amount of nitrogen left in a soil after 60 years of cultivation is attributable to retention of mineral N by recycling.

Fertilizer applications expressed increases in organic matter content but to a lesser degree than continuous cropping. Respective increases in total C, total N, total S contents were 10.6, 13.6 and 17.0%(Table 16). These led to slightly wider C:S ratios in the non-fertilized plots than the fertilized plots, while C:N ratios were similar in the two kinds of plots(Table 17). Long continued application of N fertilizers to two soils, one under grass and the other under arable cropping in Rothamsted also showed slight increases in organic C and organic N(Jenkinson,1981). Jenkinson(1981) therefore concluded that large quantities of inorganic N have had remarkably little effect on either the

Table 17: Effect of fallow and fertilizer on elemental ratios of C/S, C/N and N/S in the Breton plots.

Series and Plot No.	Soil No.	Plot Treatment	C/N	C/S	N/S
E3	13	Fallow, Fert	12.0	76.9	6.4
E5	14	Fallow	11.4	73.7	6.4
F3	15	Non-fallow, Fert	12.3	83.7	6.8
F5	16	Non-fallow	12.9	94.4	7.3
Mean		Fallow	11.7	75.4	6.4
Mean		Non-fallow	12.6	89.1	7.1
Mean		Fert	12.1	80.3	6.6
Mean		Unfert	12.2	84.1	6.9

Fert - Fertilized Plots

Unfert - Unfertilized Plots

amount of organic matter in the soil or its C:N ratio. This conclusion at Rothamsted is in consonance with the observation with soil samples taken from some of the Breton plots. The Breton plots like the Rothamsted plots are designed to study the effect of long-term cropping and management practices on soil organic matter. They were established about 50 years ago.

Fertilized and non-fertilized plots exhibited the same close relationship between C and N but divergent relationship between S and C similar to observations made in the fallow and non-fallow plots. In contrast to the effect of non-fallowing, S accumulated at a faster rate than C and N with fertilization. This is shown by higher increases in S content in relation to C and N (Table 16) and lower N:S and C:S ratios of fertilized plots than non-fertilized plots(Table 17). Probably losses due to applied N were higher than those for applied S or in relation to plant requirements, the application rate of S to these plots is relatively greater than that of N(Table 1). Plant requirements for N are generally higher than that for S. Additionally, denitrification will contribute to more losses of N than S especially on the fallow plots. The faster rate of accumulation of S than N appears to be consistent with the view expressed by McGill and Cole(1981) that in situations where S is added abundantly it should be possible to store as sulphate esters(C-O-S), thus allowing S to accumulate faster than N. Table 18 shows that percentages of

Table 18: Amounts of total S, C-O-S, C-S and C-O-S:C-S ratios in virgin soils of the Chernozemic Order and cultivated soils of the Breton plots.

Great Group And Soil Type	Total S ug/g soil	C-O-S ug/g soil	C-S ug/g soil	C-O-S /C-S
Black				
Ellerslie	1187	893(75)	294.0(24)	3.0
Ponoka	397	266(67)	130.6(32)	2.0
Dark Brown				
Lethbridge	566	413(72)	153.4(27)	2.7
Standard	504	337(67)	166.6(33)	2.0
Brown				
Chin	380	241(63)	139.1(36)	1.5
Vauxhall	360	213(59)	147.2(40)	1.5
Gray Luvisol				
Breton E 3	173	93(53)	79.7(46)	1.0
Breton E 5	151	68(44)	83.7(55)	0.8
Breton F 3	252	157(62)	94.3(37)	1.7
Breton F 5	211	106(50)	104.7(49)	1.0

N.B--Values in parentheses indicate percentages of total S found as C-O-S and C-bonded S in the various soils.

total S occurring as C-O-S was higher in fertilized plots(E3 and F3) than in non-fertilized plots(E5 and F5). Freney et al. (1975) also found that plants derived a greater part of their indigenous S from C-bonded S, but in the case of labelled S(essentially S incorporated into the organic matter from recently applied fertilizer) however, the greater part was incorporated into the C-O-S fraction and it was from this fraction that plants derived most of the labelled S taken up.

Most agricultural soils have N:S ratios in the range of 6.6 to 10.1(Freney and Williams, 1980). N:S ratios calculated from data of Dormaar and Webster(1963) fall within this range. The N:S ratios of soils from the Dark Brown and Brown soil zones in the present study including soils from sites(Chin and Lethbridge) similar to those used by Dormaar and Webster(1963) are however below this range(Table 15). The lower N:S ratios found in the present study than those in Dormaar and Webster's study are due to higher total S contents found in soil samples in the present study. This could be attributed to the more sensitive method of sulphate determination used in the present study. Dormaar and Webster(1963) determined sulphate obtained from total S extracts turbidimetrically as barium sulphate. In the present study, preliminary investigation showed that analyses of soil extracts turbidimetrically gave lower total S values than those obtained with the Inductively Coupled Plasma. However, similar low ratios have been found in

surface soils from Oklahoma(Harper, 1959), Iowa(Tabatabai and Bremner, 1972) and Brazil (Neptune et al., 1975).

One of the objectives of this study was to test some of the hypotheses flowing from McGill and Cole's model on C,N,S and P relationships in soils. The major hypothesis of lack of stoichiometry between N and S behaviour in soils is consistent with data mainly from the Breton plots' soil samples and with some soil samples from the Chernozemic Order. Minor hypotheses from the model are that firstly along a climosequence of soils or upon cultivation of virgin soils, ratios of N:S should change inversely with ratios of C-O-S:C-bonded S because of the closer link between N and C-bonded S than C-O-S. Secondly in S deficient soils, the ratio of C-O-S:C-bonded S should drop dramatically due to rapid utilization of sulfate esters under stress conditions and the weak association of sulfate esters with the remainder of the humic component.

Examination of N:S ratios and C-O-S:C-S ratios of virgin soils showed that in general the N:S ratios were inverse to to those of C-O-S:C-S.(Fig. 7). In the soil samples from the Breton plots, however, a direct relationship was observed between N:S and C-O-S:C-S ratios from the fallow plots to the non-fallow plots(Table 19). Probably the most consistent and significant trend observed is that ratios of C-O-S:C-S decreased with decreasing amounts of total S, in both the virgin soils of the Chernozemic Order and the cultivated soils of the Breton

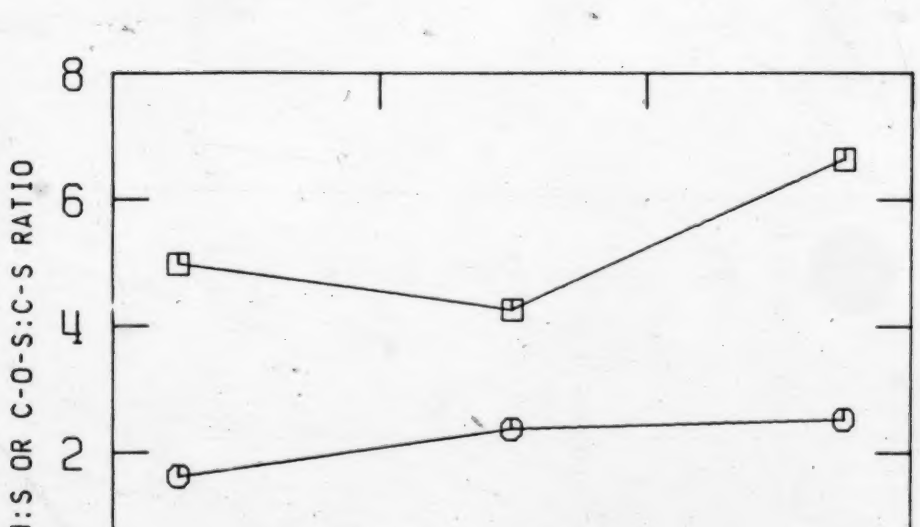

FIG. 7. RELATIONSHIP BETWEEN N:S AND C-O-S:C-S RATIOS IN VIRGIN CHERNOZEMIC SOILS.

N:S -----
C-O-S:C-S ----

Table 19: Effect of fallow and fertilizer(fert) on elemental ratios of N:S and C-O-S:C-S in the Breton plots.

Series and Plot No.	Soil No.	Plot Treatment	N/S	C-O-S/C-S
E3	13	Fallow, Fert	6.4	1.2
E5	14	Fallow	6.4	0.8
F3	15	Non-fallow, Fert	6.8	1.7
F5	16	Non-fallow	7.3	1.0
Mean		Fallow	6.4	1.0
Mean		Non-fallow	7.1	1.4
Mean		Fert	6.6	1.4
Mean		Unfert	6.9	0.9

plots. (Table 18). This would appear to be consistent with the second minor hypothesis of the model, i.e. ratios of C-O-S:C-S should diminish in severely restricted systems.

Soil samples from Ellerslie and Lethbridge sites were the only soil samples which showed decreases in all three nutrients, i.e. total C, total S and total N when the vigin soils were brought under cultivation. Discussion of the relationships between the various organic matter components would therefore be limited to data from these two soils and the Breton plots. N/S ratio of Ellerslie cultivated soil was wider than the corresponding virgin soil, but the reverse was observed with the samples from Lethbridge(Table 20). This showed that S was depleted faster than N at Ellerslie but slower than N at Lethbridge upon cultivation. Harper(1959) had also observed that slightly more than half (55%) of cropped Oklahoma soils had a narrower N:S ratio than the corresponding virgin soil. C-O-S and C-bonded S contents of soils from Ellerslie and Lethbridge sites were lower in the cultivated soils than in the virgin soils. In these Chernozemic soils therefore C-bonded S fraction mineralized or accumulated at faster rates than the the C-O-S fraction, i.e. a higher proportion of total S mineralized came from C-bonded S. This is shown by the wider C-O-S/C-S ratios (Table 20) and higher percentage losses of C-bonded S than C-O-S when the virgin soils were cultivated(Table 21). Analogous findings have been reported(McLachlan and De Marco,1975; McLaren and

Table 20: Effect of cultivation on elemental ratios of N:S and C-O-S:C-S in Ellerslie and Lethbridge soils.

Soil Type	N/S	C-O-S/C-S
Ellerslie Virgin	6.7	3.0
Ellerslie Cultivated	7.2	3.7
Lethbridge Virgin	4.4	2.7
Lethbridge Cultivated	3.4	3.1

Table 21: Effect of cultivation and fallowing on amounts of C-O-S, C-S, No, Total S and Total N in soils.

	ug g⁻¹ soil									
	C - O - S		C - S		No		Total S		Total N	
Soil	VN	CF	VN	CF	VN	CF	VN	CF	VN	CN
Ellerslie	893.0	578.5	294.0	154.0	285.7	147.1	1187.0	732.5	7928.1	5267.5
Decrease*(%)		35.2		47.6		48.5		38.3		33.6
Lethbridge	413.0	366.0	153.4	118.4	240.4	99.4	566.4	484.4	2503.9	1666.9
Decrease*(%)		11.3		22.8		58.7		14.5		33.4
Breton Plots+	132.1	80.7	99.5	81.7	101.8	67.7	231.6	162.4	1630.0	1041.6
Decrease*(%)		39.2		17.8		33.5		29.9		36.1

Key:

VN - Virgin or non-fallow soils

CF - Cultivated or fallow soils

* - Values are expressed as percentages of the differences in C-O-S, C-S, No, total S, and Total N between virgin or non-fallow and cultivated or fallow soils respectively.

\+ - Entries are means of two values.

Swift,1977). McLaren and Swift(1977) however postulated that it is unlikely that C-bonded S will be converted directly to sulphate, but rather it will pass through a C-O-S form prior to release as inorganic sulphate.

In contrast to soil samples from the Ellerslie and Lethbridge sites, soil samples from the Breton plots showed that greater proportions of total S mineralized or accumulated came from the C-O-S pool(Table 21).

If similar reasonings used to explain relative No and total N losses in the soil samples from the two orders are extended to S losses, these contradictory observations would tend to make the C-bonded S fraction more active in relation to the C-O-S fraction. The more active fraction depletes at a faster rate than the less active fraction at the initiation of cultivation, while the converse is true as steady state conditions are approached(McGill,1983). Subsequently, C-bonded S losses were more than C-O-S losses in the Chernozemic soils(Ellerslie and Lethbridge), since these appear to be further away from their steady state than the Luvisolic soils, due to their lesser degradation rates. These losses are therefore reversed in the Luvisolic soils, where the soils appear to be closer to steady state conditions. The behaviour of C-bonded S is thus similar to that of potential mineralizable N.

C-bonded S depleted faster than total S with cultivation in both the Ellerslie and Lethbridge soils. Similarly, in these two soils No was depleted at faster

rates than total N(Table 21). In the soil samples from the Breton plots, losses due to total S and total N were higher with summerfallowing than those due to C-bonded S and No respectively(Table 21). In contrast, percentage losses due to C-O-S fraction were higher and lower than those due to total S in soil samples from the Breton plots and Chernozemic order respectively. Generally, it appears that th behaviour of C-O-S followed that of total S more closely than C-bonded S. This is consistent with relationships involving these three components of organic matter as predicted by McGill and Cole's(1981) model. The behaviour of C-O-S than that of C-bonded S was found to be more closely linked with total N. This contradicts one of the hypothesis of McGill and Cole's(1981) concept that C-bonded S and not C-O-S will follow total N more closely. This study showed that there appears to be an intimate ralationship between the behaviours of No and C-bonded S and not total N and C-bonded S.

An exception was observed in soil samples from the Breton plots following fertilizer additions. Fertilizer additions led to increases in both No and the ratio of No/N, while both the C-bonded S content and proportions of total S as C-bonded S decreased(Table 7 and 22). Increases were observed in C-O-S and total S contents and S accumulated at a faster rate than N(Table 22).

It appears that correlation coefficients between soil properties do not reveal the true relationships in their

Table 22: Effect of Fertilizer Applications on Soil Properties (Breton Plots).

Type of Rotation	Total C		Total N		Total S		No.		C-O-S		C-S	
	%								ug g^{-1} soil			
	NF	F	NF	F	NF	F	NF	F	NF	F	NF	F
Wheat-Fallow	1.12	1.33	0.098	0.111	0.015	0.017	50.5	82.4	68.0	93.4	83.7	79.7
Continuous Cropping	1.99	2.11	0.154	0.172	0.021	0.025	91.2	112.4	106.3	157.8	104.7	94.3
Mean	1.56	1.72	0.126	0.142	0.018	0.021	70.8	97.4	87.2	125.6	93.7	87.0
*Change(%)	+10.3		+12.7		+16.7		+37.3		+44.0		-7.6	

* Increases or decreases due to fertilizer application. Values are expressed as percentages of mean differences in amounts of total C, total N, total S, No, C-O-S and C-S between fertilized plots and non-fertilized plots.

NF - non-fertilized plots.

F - Fertilized plots.

Table 23: Correlation coefficients between pairs of properties in the Breton plots and Ellerslie and Lethbridge sites.

	Total C	Total N	No	C-O-S	C-S
Total S	0.956	0.957	0.870	0.998	0.966
C-S	0.943	0.943	0.894	0.948	
C-O-S	0.950	0.951	0.855		
No	0.782	0.796			
Total N	0.999				

behaviour. As indicated in Table 23, similar correlation coefficients were observed among all the components of organic matter examined. These significant correlations may merely reflect the general relationship which exists between organic matter components and soil organic C as a whole(Lee and Speir, 1979). The correlation coefficents observed in this study do not seem to reflect the differences or similarities in behavioural patterns observed among the various organic matter components from the Chernozemic order (i.e. Ellerslie and Lethbridge) and the Breton plots.

V. CONCLUSIONS

Different mineralization time curves were obtained for organic N and S mineralization with two methods of incubation. Mineralization time curves were irregular with the continuous incubation method for both organic S and organic N. Cumulative amounts of N and S mineralized using the incubation and leaching technique were curvilinear and linear, respectively, with time of incubation.

Mineralization studies using the continuous incubation method have been criticised for various reasons. Stanford and Smith(1972) stated their N-mineralization time curves obtained seldom provided a rational or consistent basis for estimating long-term N-supplying capacities of soils. The reliabilty of results derived from extended incubations in such static, closed systems is questionable(Stanford, 1982) and Tabatabai and Al-Khafaji (1980) felt that it does not show the true trend of S mineralization in soils, while the leaching and incubation technique seems to simulate the removal of mineral N and S by plants and leaching processes of these elements under field conditions. Results from this study are consistent with the above views.

Data from the incubation and leaching experiments showed that the mineralization of organic N followed a first order reaction kinetics and can be represented by the equation $-dN/dt=kN$. In contrast the mineralization of organic S by the leaching and incubation technique followed zero order kinetics and can be represented by the equation

-dS/dt=k. A labile fraction thus appears to exist for organic N but not for organic S. Alexander(1977) made a similar conclusion from works of Tabatabai and Bremner(1972) and Freney et al.(1975). This will be further corroborated by the finding in this study that amounts of cumulative S mineralized was almost equally well correlated with amounts of total S, C-bonded S and C-O-S(Table 3).

The significance of the different orders of reaction obtained for these two elements further indicated that a mineralizable pool for organic N but not for organic S can be estimated by the procedure described by Smith et al.(1980) and Talpaz et al.(1981). Significant amounts of organic N were leached out concurrently with mineralized N at the end of each incubation period with the incubation and leaching technique. The mineralizable pool or N mineralization potential(No) estimated using only mineral N leached ranged from 53.7 to 85.2% of No estimated with total N leached. These observations substantiate the finding of Smith et al.(1980) that the ignoring of organic N leached can lead to serious errors in the determinations of N mineralization potentials and N mineralization rate constants for aerobically incubated soils. Though no attempts were made to determine if any forms of organic S were leached out also, it can be presumed that if it did occur it would be in insignificant amounts. The linear relationship of cumulative S mineralized will give support to this presumption, since leaching of any form of

mineralizable organic S will tend to lower subsequent values for S mineralization rates. Both the N mineralization rate constant(k) and the potentially mineralizable N, No, were affected by soil forming factors and management practices. Increases and decreases were found in k and No estimates respectively from the Black to the Brown soil zone. The No/N ratio did not follow any of these two parameters but appeared to be affected by texture. The Dark Brown soils with the highest clay content had the highest proportion of total N in this phase. Cultivation led to decreases in both No and active fraction of of total N, but to increases in k estimates in the Chernozemic soils.

In the Breton plots, mean k value and active fraction were higher and mean No estimates were lower in the fallow plots than the non-fallow plots. These observations are related to different cropping practices on these plots.

Losses of No and C-bonded S with cultivation were greater than losses of total N and total S respectively in the Chernozemic soils. Due to the inconsistent behaviour of total S upon cultivation, the observations with respect to total S and C-bonded S are limited to only soils from Ellerslie and Lethbridge. Only these two soils showed decreases in all three major fractions elements, i.e total C, total N and total S upon cultivation. In the Breton plots, losses due to total N and total S were greater than those of No and C-bonded S respectively with summerfallowing.

These two contrasting observations in soils from the two orders may reflect differences in proximity of the cultivated soils from their respective steady states(McGill,1983). Faster degradation rates upon cultivation in Luvisolic soils than Chernozemic soils will be enhanced by summerfallow practices. Hence, soils from the Breton plots will move towards steady state conditions faster than soils from the Chernozemic Order. Mineralizable components of soil organic matter are depleted at faster rates than total organic matter and therefore tend to reach steady state conditions faster than total soil organic matter(McGill,1983). As this state is approached removals and additions rates are almost equal. Thus a greater proportion of total N and total S was found to be active (No/N) and occuring as C-bonded S fraction(C-S/S) respectively in: (i) soil samples from the Breton fallow plots than those from the non-fallow plots and;(ii) in soil samples from the Breton plots than those from the Chernozemic cultivated sites.

The behaviour of C-bonded S thus followed closely that of the potential mineralizable, No and not total N. C-O-S was observed to follow total S and total N more closely than C-bonded S. Losses due to C-bonded S were higher than those due to C-O-S in the Chernozemic soils. In Breton plots these losses were reversed. Though these observations suggested that C-bonded S is more labile than C-O-S or HI-reducible S fraction the contributions to S mineralization upon

cultivation from sulphate esters cannot be ignored. Bettany et al.(1979) had earlier noted that the usual fractionation of total soil organic S into sulphate esters and C-bonded S is simply not selective enough for any meaningful interpretation, since both fractions seem to contribute significant amounts of S to the plant available pool form through mineralization reactions. There also appears to be a ready conversion of S between the two fractions. (Freney et al.,1971; McLaren and Swift,1977). Evidence for this conversion is, however, indirect and therefore inconclusive. Observations from long-term effect of natural mineralization processes on organic S fractions distributions are in conflict with deductions made from results obtained from the leaching and incubation technique on S mineralization in this study. While results from the latter technique suggested the absence of a labile fraction for S, the former showed that though the two recognised forms of S both contribute to S mineralization with cultivation, the C-bonded S fraction is more labile than the C-O-S fraction. Probably the initial rates of mineralization of C-bonded S and C-O-S are almost the same and differences can only be observed after long periods of incubation. Thus an incubation experiment period of about five months as used in this study might be rather too short for any meaningful differences in the mineralization rates of the two fractions to be detected.

More significantly, results from this study further confirm earlier conclusions that although N and S mineralization have similarities, they are not parallel metabolic processes and are not released in the same ratio as they occur in the organic matter(Kowalenko and Lowe,1975; Swift,1976; Tabatabai and Al-Khafaji,1980; McGill and Cole,1981).

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VII. APPENDIX

'APPENDIX TABLES'

Table A: Net. Cumulative Mineralized N (ug N g^{-1} Soil) and Total N Leached (ug N g^{-1} Soil) After Specified Days of Incubation. Entries are Means of Three Replicates ± Standard Deviations.

Soil	Expt	14 Days	28 Days	42 Days	56 Days	70 Days	84 Days	98 Days	112 Days	126 Days	140 Days	154 Days
Ellerslie Virgin	CI	13.9±0.2	27.0±2.5	35.9±2.5	49.0±1.2	53.8±0.8	69.5±1.3	83.0±6.8	89.3±1.7	105.9±4.2	136.0±3.5	
	(A) IL	21.2±2.3	48.1±1.0	66.8±0.5	83.3±1.0	100.9±3.6		130.2±3.6		152.2±3.9		166.5±7.0
	(B)	32.0±1.9	61.8±2.0	83.4±2.7	104.4±2.2	126.6±7.4		160.4±6.3		187.2±4.1		205.7±6.0
Ellerslie Cultivated	CI	9.6±4.0	8.0±4.1	19.0±1.2	21.9±2.0	20.0±2.6	30.2±1.7	32.5±2.4	37.6±1.3	41.9±1.2	68.7±7.8	
	(A) IL	8.6±0.2	22.7±1.1	34.5±1.3	41.1±1.5	48.2±1.5		62.7±2.2		69.9±1.9		81.6±3.5
	(B)	15.5±0.6	33.2±1.6	47.6±3.5	57.3±2.0	67.0±6.0		82.9±4.4		96.4±3.8		111.2±2.4
Ponoka Virgin	CI	6.3±0.9	15.4±1.3	18.7±3.1	26.6±2.5	28.5±1.8	35.9±2.9	46.3±0.9	51.3±7.0	52.6±3.8	76.0±2.2	
	(A) IL	7.8±0.4	19.1±3.3	27.8±2.8	35.6±3.6	39.4±7.0		56.7±2.3		66.7±2.9		76.6±2.8
	(B)	17.6±1.3	33.1±4.5	47.3±5.5	55.0±6.4	67.1±7.7		85.7±7.6		108.0±8.2		120.8±3.4
Ponoka Cultivated	CI	6.7±0.9	16.8±1.6	24.2±0.7	32.4±1.5	31.5±1.9	36.3±1.6	43.5±3.3	49.6±0.9	53.2±2.1	72.5±1.9	
	(A) IL	13.1±1.4	28.2±7.5	35.5±7.9	40.8±7.5	45.8±6.9		61.2±6.1		70.8±5.6		82.0±5.6
	(B)	21.4±2.2	37.4±4.5	44.7±4.7	52.9±6.0	64.2±6.8		83.0±6.6		100.1±7.2		107.0±1.2
Lethbridge Virgin	CI	21.1±2.0	32.6±1.5	43.0±2.8	50.1±1.3	48.2±3.1	53.6±4.7	63.4±4.3	70.5±1.7	70.2±1.2	87.6±1.0	
	(A) IL	25.3±0.7	46.4±0.7	64.3±1.7	76.4±2.0	89.4±2.2		112.6±2.2		130.9±4.5		149.4±5.3
	(B)	33.7±1.5	57.4±0.3	69.7±3.7	81.3±4.3	111.8±1.7		133.1±2.5		159.5±3.3		180.2±4.7
Lethbridge Cultivated	CI	12.5±0.7	14.0±0.6	20.6±1.1	28.2±1.3	25.3±2.0	30.7±8.9	40.1±3.6	36.9±0.8	43.1±1.2	46.8±2.1	
	(A) IL	13.3±1.1	21.4±1.5	26.4±2.2	31.8±2.9	36.9±3.7		46.0±3.4		53.1±3.5		62.3±3.1
	(B)	22.1±2.0	34.2±2.1	41.8±2.0	49.2±1.7	54.9±2.1		66.7±0.9		78.2±0.5		89.4±1.1
Standard Virgin	CI	7.7±1.7	14.1±0.4	13.1±4.4	12.7±3.2	23.9±1.7	26.6±0.3	30.5±2.0	31.4±4.9	36.3±3.6	51.8±3.4	
	(A) IL	6.1±1.7	20.6±1.9	26.4±3.4	30.9±5.3	36.8±5.6		50.8±3.4		59.6±2.7		69.2±1.9
	(B)	15.6±0.4	33.8±2.6	37.8±4.7	49.7±6.7	58.7±1.5		76.0±1.5		90.8±1.3		102.5±2.1

Table A: (con't)

Soil	Expt	14 Days	28 Days	42 Days	56 Days	70 Days	84 Days	98 Days	112 Days	126 Days	140 Days	154 Days
Standard Cultivated	CI	23.7±2.0	25.5±1.8	39.8±0.9	40.3±2.6	43.0±2.0	39.4±1.1	29.1±3.5	50.3±3.6	60.3±1.8	67.6±2.1	
	(A) IL	14.6±1.2	26.9±4.2	35.2±4.1	40.2±0.4	45.0±3.8		59.0±4.3		71.1±6.2		82.0±7.9
	(B)	23.1±1.4	38.4±4.6	47.7±5.0	59.3±8.9	63.3±6.5		81.0±7.2		98.1±8.1		113.1±11.5
Chin Virgin	CI	10.3±1.0	13.9±0.7	18.5±0.4	18.3±0.3	21.9±1.1	24.7±2.5	28.0±1.4	32.1±4.6	32.9±4.3	50.0±2.3	
	(A) IL	6.8±0.6	16.1±1.2	19.8±0.9	23.5±1.4	27.5±1.6		31.5±0.8		34.6±0.6		38.8±0.7
	(B)	14.2±2.7	28.5±2.0	34.2±2.0	39.3±1.6	46.1±0.7		54.3±1.3		61.2±0.9		67.8±5.7
Chin Cultivated	CI	7.9±0.8	5.5±1.6	11.2±2.3	9.9±1.5	16.0±1.5	14.5±2.2	16.9±1.8	17.6±2.6	15.1±1.0	30.9±2.0	
	(A) IL	3.7±1.3	12.1±2.3	16.5±1.6	18.5±1.0	19.8±2.4		24.9±3.3		27.1±3.6		32.2±4.2
	(B)	9.5±1.1	19.1±2.3	25.2±1.6	27.8±1.1	31.9±1.4		40.0±2.5		43.0±2.8		49.1±3.1
Vauxhall Virgin	CI	10.1±0.4	15.2±1.4	19.0±1.2	16.3±0.8	23.0±0.9	25.3±1.7	28.0±2.1	32.7±1.9	31.2±1.6	47.6±0.9	
	(A) IL	10.3±1.6	18.6±1.8	24.6±2.4	29.5±2.1	34.5±2.8		41.4±1.1		45.3±2.3		47.6±1.9
	(B)	17.5±1.9	28.4±2.0	35.8±2.2	42.8±2.3	51.3±3.3		62.4±3.7		70.7±4.2		77.1±3.9
Vauxhall Cultivated	CI	8.5±1.7	10.7±2.2	8.8±0.5	9.9±0.6	7.9±0.5	11.9±0.6	13.2±1.1	16.5±1.9	22.5±2.2	25.4±2.1	
	(A) IL	3.9±0.6	12.5±1.5	16.5±1.2	19.0±1.3	21.2±1.7		24.5±2.6		25.5±2.7		26.2±2.6
	(B)	7.9±1.4	10.8±1.6	22.4±1.8	24.7±2.0	30.0±2.1		38.7±2.8		42.1±3.4		44.3±3.6
Breton Series E Plot 3	CI	4.3±1.6	4.5±0.4	14.1±0.5	10.9±1.1	13.9±2.0	13.8±3.1	14.5±2.5	19.7±0.8	22.4±1.1	33.6±0.9	
	(A) IL	4.4±0.9	16.7±0.7	19.9±0.8	21.6±0.9	27.8±2.3		33.5±1.6		39.1±2.5		44.2±4.2
	(B)	8.4±0.8	22.2±1.3	26.2±1.9	33.2±3.1	37.4±4.3		48.3±3.5		56.4±2.6		64.0±4.2
Breton Series E Plot 5	CI	5.3±1.1	3.3±0.7	8.6±1.7	6.6±1.3	7.5±1.5	7.2±1.8	9.8±2.7	10.4±1.6	14.8±2.0	20.9±3.6	
	(A) IL	3.7±0.7	12.5±0.4	14.2±0.1	16.4±0.5	19.9±0.6		23.5±2.5		24.7±2.2		25.8±2.0
	(B)	5.5±1.0	16.6±0.6	20.0±1.9	23.4±2.5	28.9±2.4		35.3±4.4		38.0±4.1		43.1±3.9

Table A: (con't)

Soil	Expt	14 Days	28 Days	42 Days	56 Days	70 Days	84 Days	98 Days	112 Days	126 Days	140 Days	154 Days
Breton Series F Plot 3	CI	10.1±1.1	11.7±0.9	21.9±1.2	26.1±0.9	33.5±1.0	36.3±6.0	44.8±5.6	48.2±1.3	56.1±3.9	68.6±3.9	
	IL (A)	6.8±0.8	19.3±0.5	27.1±2.9	33.7±1.9	41.8±1.9		50.8±2.9		59.0±3.6		62.6±3.5
	IL (B)	12.8±0.7	26.4±1.2	35.9±2.2	41.5±2.0	57.0±2.3		69.1±0.8		79.0±1.0		83.8±5.6
Breton Series F Plot 5	CI	2.9±0.6	8.7±0.6	13.9±1.2	17.2±0.4	19.4±0.9	22.0±0.2	27.8±1.4	26.1±4.2	40.0±2.8	46.2±3.6	
	IL (A)	5.7±0.7	16.2±1.8	20.4±1.6	23.3±1.6	29.6±1.9		38.3±2.8		43.6±1.0		44.6±0.9
	IL (B)	11.6±2.6	24.9±2.9	32.3±2.5	34.3±1.7	45.6±6.0		53.8±2.6		65.6±3.5		71.0±3.1

Key:

CI - Continuous Incubation

IL - Incubation and Leaching

A - Cumulative N Mineralized

B - Total N Leached

Table 8: Net or Cumulative S Mineralized (ug S g^{-1} Soil) After Specified Times of Incubation. Entries are Means of Three Replicates and Standard Deviations.

Soil	Expt	14 Days	28 Days	42 Days	56 Days	70 Days	84 Days	98 Days	112 Days	126 Days	140 Days	154 Days
Ellerslie	CI	-0.8±0.5	0.8±0.2	1.0±0.5	3.4±2.0	1.4±0.8	3.4±0.2	5.8±0.9	6.0±2.5	8.1±1.2	8.6±0.6	
Virgin	IL	1.6±0.3	3.4±0.2	4.9±0.3	6.8±0.4	8.5±0.4		12.3±0.4		14.9±0.2		17.9±1.2
Ellerslie	CI	2.2±0.5	0.2	1.6±0.2	2.4±0.9	1.8±0.8	2.6±0.3	3.0±1.2	6.1±1.1	5.5±0.4	8.7±0.6	
Cultivated	IL	0.7±0.1	1.6±0.2	2.1±0.3	2.7±0.4	3.5±0.4		4.8±0.5		5.8±0.4		8.2±0.1
Ponoka	CI	0.0	0.6±0.2	0.3±0.1	1.3±0.2	0.7±0.5	1.4±0.1	1.2±0.7	3.6±0.3	4.4±0.5	4.5±0.7	
Virgin	IL	0.5±0.0	1.2±0.0	1.8±0.1	3.1±0.9	4.2±0.7		5.8±0.6		6.9±1.0		8.5±0.3
Ponoka	CI	-0.4±0.1	0.9±0.3	0.4±0.2	0.4±0.1	1.5±0.7	0.3±0.1	1.5±0.4	3.5±0.5	4.2±1.1	5.4±1.3	
Cultivated	IL	0.6±0.1	1.7±0.2	2.3±0.3	3.0±0.4	4.0±0.3		5.8±0.5		6.9±0.5		8.5±0.3
Lethbridge	CI	-0.4±0.1	0.1	3.0±0.2	4.0±0.4	4.0±0.1	4.2±1.2	4.1±0.9	8.0±1.4	8.9±1.0	10.7±1.9	
Virgin	IL	0.6±0.1	2.2±0.6	4.0±0.4	5.6±0.7	7.5±0.4		10.6±0.4		13.1±0.5		17.0±0.5
Lethbridge	CI	1.0±0.6	0.7±0.4	3.7±1.6	3.2±1.2	2.9±1.3	2.6±0.2	3.6±0.5	5.4±0.9	7.3±1.0	5.1±2.4	
Cultivated	IL	0.5±0.0	1.0±0.0	1.6±0.1	2.5±0.1	2.9±0.3		4.3±0.6		5.6±0.8		7.4±1.2
Standard	CI	0.0	0.6±0.3	0.9±0.4	0.6±0.3	1.2±0.2	1.5±0.9	3.1±0.3	3.8±1.1	3.0±1.0	5.2±0.5	
Virgin	IL	0.5±0.0	1.4±0.2	2.1±0.3	3.3±0.5	3.9±0.3		5.9±0.6		7.2±0.5		9.0±0.5
Standard	CI	-3.0±1.0	8.1±3.5	2.5±0.2	15.1±4.4	9.9±5.6	8.9±2.4	2.3±0.5	-3.1±0.6	-4.4±0.5	-6.2±0.6	
Cultivated	IL	14.8±1.2	20.5±1.1	22.7±1.2	25.6±1.7	28.8±2.6		32.3±2.3		34.7±2.1		37.6±0.4
Chin	CI	0.2±0.07	0.4±0.06	0.3±0.0	0.3±0.2	0.3±0.2	0.8±0.0	0.7±0.5	1.7±0.5	1.0±0.2	1.2±0.4	
Virgin	IL	0.6±0.1	1.1±0.1	1.5±0.2	2.0±0.2	2.4±0.2		3.3±0.3		3.8±0.3		4.7±0.3
Chin	CI	0.0	0.2±0.0	0.3±0.0	0.0	0.1±0.0	0.7±0.6	0.5±0.1	0.9±0.3	0.4±0.3	1.2±0.0	
Cultivated	IL	0.5±0.0	0.9±0.0	1.4±0.1	1.7±0.0	2.2±0.1		3.3±0.2		3.7±0.2		4.6±0.7
Vauxhall	CI	0.1±0.0	0.6±0.2	0.2±0.0	0.0	0.2±0.0	0.7±0.1	0.5±0.1	1.0±0.2	1.1±0.4	1.2±0.0	
Virgin	IL	1.0±0.2	1.6±0.3	2.1±0.4	2.7±0.4	3.4±0.5		4.6±0.6		5.8±0.8		7.0±0.6

Table B: (con't)

Soil	Expt	14 Days	28 Days	42 Days	56 Days	70 Days	84 Days	98 Days	112 Days	126 Days	140 Days	154 Days
Vauxhall	CI	0.6±0.2	0.7±0.4	0.2±0.1	0.6±0.3	0.1±0.0	1.0±0.0	1.1±0.3	1.1±0.1	1.1±0.4	1.2±0.2	
Cultivated	IL	0.8±0.3	1.3±0.5	1.9±0.3	2.4±0.5	3.0±0.6		3.8±0.7		4.5±0.5		5.2±0.6
Breton Series E Plot 3	CI	0.0	0.6±0.1	0.7±0.4	0.3±0.2	0.3±0.2	1.2±0.5	1.8±0.4	1.7±0.4	1.2±0.5	0.3±0.1	
	IL	0.7±0.1	1.2±0.1	2.2±0.1	3.0±0.5	3.5±0.5		4.8±0.5		5.7±0.4		7.4±0.3
Breton Series E Plot 5	CI	0.1±0.0	0.2±0.1	0.1±0.0	0.2±0.1	0.3±0.1	0.7±0.3	0.6±0.2	0.7±0.2	0.5±0.1	0.4±0.2	
	IL	0.7±0.1	1.1±0.2	1.5±0.3	2.0±0.1	2.4±0.1		3.7±0.3		4.4±0.3		5.0±0.4
Breton Series F Plot 3	CI	2.4±0.8	1.5±0.7	1.6±0.4	1.8±0.8	1.6±0.6	2.5±1.2	4.6±0.6	3.5±0.8	3.6±0.6	3.4±0.7	
	IL	0.9±0.3	2.3±0.1	2.9±0.2	4.0±0.2	4.9±0.3		6.8±0.4		8.2±0.2		10.1±0.4
Breton Series F Plot 5	CI	0.0	0.5±0.05	0.6±0.2	0.7±0.1	0.2±0.05	0.6±0.2	1.0±0.1	1.6±0.2	1.4±0.2	1.3±0.1	
	IL	0.6±0.1	1.2±0.2	1.9±0.2	2.7±0.4	3.6±0.5		5.3±0.9		6.8±0.9		8.5±0.6

Key:

CI - Continuous Incubation

IL - Incubation and Leaching